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EXCHANGEABLE CALCIUM AND POTASSIUM IN SOILS AS AFFECTED BY CROPPING AND FERTILIZATION

BENJAMIN D. WILSON

Cornell University

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Investigations dealing with the presence and the quantity of exchangeable cations in soils have led to the general conclusion that in most humid soils calcium is the predominant exchangeable cation. Such studies have also shown that magnesium, potassium, and sodium are usually held in exchangeable form in relatively small amounts and that the quantity of magnesium commonly exceeds those of potassium and sodium.

As a result of these experiments, which have been reviewed repeatedly in the literature, investigators have turned their attention to the effect of certain practices on the exchangeable cations of the soil. Page and Williams (8), in reporting the content of exchangeable cations in certain of the soils at Rothamsted, were among the earlier workers in this field. More recently Humfeld (3), Merkle (5), Martin (4), Metzger (6), and others have reported results to show the effect of cropping and fertilizer treatment on the removal or the accumulation of exchangeable cations in soil.

The results of some of these studies will be discussed later in connection with the findings of the present investigation, which is concerned primarily with the effects that cropping, limestone, and mineral fertilizers have exerted on the exchangeable calcium and potassium in a number of soils. In addition, consideration is given to the relation of the exchangeable calcium found in the soils to their colloidal content and hydrogen-ion concentration.

SOILS OF THE INVESTIGATION

Six soils were employed in the investigation. Soils representative of three different soil types, designated as Dutchess silt loam, Volusia silt loam, and Ontario loam, were collected from each of two localities in New York. Certain facts concerning the soils are shown in table 1. All of them originated from the weathering of glacial till and are of rolling topography. But, as the table shows, their fertility is distinctly different.

The soils were collected to a depth of 3-feet, the soil of each foot being thoroughly mixed and maintained as a separate lot. The resulting samples were brought to Ithaca and placed in iron cylinders 2 feet in diameter and 3 feet deep. These had been previously placed in the ground with their upper rims

slightly above the surface of the soil. This was accomplished by placing the cylinders in a long narrow trench excavated for the purpose and later filling in the spaces around and between them with soil. The cylinders were open at the bottom with native subsoil acting as a base.

The several lots of soil were placed in the cylinders in the same relative position as the soil had existed in nature, the soil of the third foot being placed in the bottom portion of the cylinders, the soil of the second foot next in order, and the soil of the first foot in the upper portion of the cylinders. The soils were exposed to natural weather conditions.

MANURIAL TREATMENT AND CROPPING SYSTEM

Nine cylinders were filled with each of the six soils. Some of the soils of each set of cylinders received manurial treatment; others remained untreated. Only three of the treatments (shown in table 2) will be discussed here.

The first four soils listed in the table received the same application of nitrate of soda, acid phosphate, and muriate of potash. Because of their greater fertility, the two remaining soils received a somewhat smaller treatment of the three fertilizers. Limestone was applied to each of the soils at the beginning of the experiment in sufficient quantity to satisfy its lime requirement to a depth of 1 foot as determined by means of the Veitch method. Three additional applications of limestone were made during the course of the experiment, or in those years when the soil was planted to clover. Fertilizers were applied annually. Nitrogen was withheld, however, in the years that clover appeared in the rotation. The cropping system consisted of a 4-year rotation of fodder corn, timothy, barley, and clover.

After 15 years the experiment was discontinued and the soils were removed from the cylinders. Each of the 3-foot levels of soil was removed separately. This could not be done by sampling to definite foot levels because the soils had settled to some extent during the period that they had remained in the cylinders. Nevertheless, the character and the appearance of the soil of the three different depths was such that a rather accurate separation on this basis was possible.

Representative samples of the soils which were taken from the upper part of the cylinders were employed in the present investigation. They were air-dried and passed through a 1-mm. sieve. Stones larger than 1 mm. were discarded.

EXCHANGEABLE CALCIUM

Exchangeable calcium was determined by means of electrodialysis. A two-compartment cell, which is described in a previous paper (10) and which was designed by Bradfield (2), was used for this purpose. The method consisted essentially in subjecting 10 gm. of soil to the influence of a direct current of 110 volts with a sliding-contact rheostat in the circuit. An alundum thimble served as a membrane. The soils were electrodialyzed for 8 hours during which

TABLE 1

Soils of the investigation

SOIL	LOCATION	pH	MATERIAL	FERTILITY
Dutchess silt loam	Orange Co.	4.28	Slate, quartzite	Medium
	Dutchess Co.	4.84		
Volusia silt loam	Tompkins Co. (Cayuta)	4.80	Shale, sandstone	Low
	Tompkins Co. (Turkey Hill)	4.98		
Ontario loam	Oneida Co.	6.83	Shale, sandstone,	High
	Monroe Co.	6.96	limestone	

TABLE 2

Total quantity of fertilizer and limestone applied to the soils of the investigation during a period of 15 years

SOIL	NUMBER OF CYLINDER	TREATMENT, POUNDS AN ACRE				SYMBOL OF TREATMENT
		Nitrate of soda	Acid phosphate	Muriate of potash	Limestone	
Dutchess silt loam	29	3,027	4,356	1,213	27,176	F L
Orange Co.	30	.....	.....	.....	27,176	L
	31	.....	.....	.....	.....	O
	32	3,027	4,356	1,213	.....	F
Dutchess silt loam	36	3,027	4,356	1,213	25,343	F L
Dutchess Co.	37	.....	.....	.....	25,343	L
	38	.....	.....	.....	.....	O
	39	3,027	4,356	1,213	.....	F
Volusia silt loam	43	3,027	4,356	1,213	22,348	F L
Cayuta	44	.....	.....	.....	22,348	L
	45	.....	.....	.....	.....	O
	46	3,027	4,356	1,213	.....	F
Volusia silt loam	50	3,027	4,356	1,213	35,854	F L
Turkey Hill	51	.....	.....	.....	35,854	L
	52	.....	.....	.....	.....	O
	53	3,027	4,356	1,213	.....	F
Ontario loam	71	2,935	4,026	1,094	4,727	F L
Oneida Co.	72	.....	.....	.....	4,727	L
	73	.....	.....	.....	.....	O
	74	2,935	4,026	1,094	.....	F
Ontario loam	78	2,935	4,026	1,094	3,006	F L
Monroe Co.	79	.....	.....	.....	3,006	L
	80	.....	.....	.....	.....	O
	81	2,935	4,026	1,094	.....	F

time the amperage varied with the different soils and decreased as the process of electrodialysis continued. It varied from approximately 100 to 2 milliamperes. Usually about 1 liter of diffusate was collected during the 8-hour period. The total cationic content of the diffusate from each soil was ascertained by titration with suitable reagents (10) and its calcium content was determined gravimetrically by means of the ammonium-oxalate method.

Carbonate was present to some extent in all of the soils. Those that had received the largest application of limestone contained the largest quantities of carbonate. Electrodialysis, as here conducted, did not remove quantitatively the calcium present as carbonate but removed it in proportion to the quantity present in the soil. It was found by determining the carbonate content of the soils before and after electrodialysis, that about 50 per cent of it was decomposed during the process.

Previous experiments (10, 11) had shown that exchangeable calcium is removed by electrodialysis from the alumino-silicic complex of soil with comparative ease and within a period of 8 hours. In view of this knowledge, it was inferred that any calcium remaining in the soils after they were electrodialyzed for 8 hours would not be present in exchangeable form. In assuming that all of the exchangeable calcium of the soils was present in the diffusates, it became necessary, in order to arrive at its value, to determine the amount of calcium in each of the diffusates which had been present in the soil in the form of carbonate.

This was done by ascertaining the quantity of carbonate lost from each of the soils during electrodialysis and calculating the resulting value to calcium equivalents. By substracting this figure from the quantity of calcium in the corresponding diffusate, a value for exchangeable calcium was obtained. Such a procedure may be questioned, for it assumes that all of the carbonate present in the soil was associated with calcium. For all practical purposes this appears to be true in the light of certain data that are to be presented. This view is strengthened also from the fact that the soils contained exceedingly small quantities of exchangeable magnesium and that the limestone which was applied to the soils contained approximately 98 per cent of calcium carbonate.

The quantity of exchangeable calcium found in each of the soils at the end of the experiment is recorded in table 3. The limestone treatments increased the quantity of exchangeable calcium in the soils of the Dutchess and the Volusia series. When the cylinders were filled, samples of the soils were air-dried and stored in closed containers. The reaction of each of these soils at the end of the experiment, or after they had been stored for a period of 15 years, was less than pH 5, as determined potentiometrically by the use of a quinhydrone electrode. Assuming that the order of their intensity did not change during storage, the soil with the greatest initial acidity, the Dutchess silt loam from Orange County adsorbed[1] relatively more calcium than did any of the other soils.

[1] The word "adsorption," as used in this paper, is not intended to distinguish between physical and chemical forces.

Limestone resulted in rendering all of the soils alkaline, as is shown in the fourth column of table 3. But there seems to be no relation between the hydrogen-ion concentration of the soils and their content of exchangeable calcium when treated with limestone. Nor does there appear to be a relation between the quantity of limestone applied to the soils and the quantity of

TABLE 3

Exchangeable calcium and potassium in the soils at the end of the experiment

(Calcium and potassium expressed in mgm. equivalents in 100 gm. of air-dry soil)

SOIL	NUMBER OF CYLINDER	TREATMENT	pH OF SOIL*	TOTAL Ca IN DIFFUSATE	Ca IN DIFFUSATE FROM $CaCO_3$	EXCHANGEABLE Ca	EXCHANGEABLE K
Dutchess silt loam	29	F L	7.2	11.52	2.79	8.73	0.66
Orange Co.	30	L	7.2	9.75	3.47	6.28	0.61
	31	O	4.7	0.65	None	0.65	0.61
	32	F	4.8	1.20	None	1.20	0.61
Dutchess silt loam	36	F L	7.4	13.10	3.66	9.44	0.56
Dutchess Co.	37	L	7.5	13.46	2.83	10.63	0.46
	38	O	5.3	3.39	None	3.39	0.41
	39	F	5.6	4.24	None	4.24	0.41
Volusia silt loam	43	F L	7.5	18.10	3.16	14.94	0.52
Cayuta	44	L	7.5	17.75	2.36	15.39	0.34
	45	O	5.3	6.50	None	6.50	0.36
	46	F	5.6	8.35	None	8.35	0.38
Volusia silt loam	50	F L	7.5	14.10	8.78	5.32	0.29
Turkey Hill	51	L	7.5	14.18	6.94	7.24	0.24
	52	O	4.9	1.80	None	1.80	0.38
	53	F	5.2	2.50	None	2.50	0.41
Ontario loam	71	F L	7.7	10.25	0.23	10.22	0.37
Oneida Co.	72	L	7.8	11.16	0.50	10.66	0.36
	73	O	6.4	10.79	0.04	10.75	0.48
	74	F	7.1	11.18	0.44	10.74	0.52
Ontario loam	78	F L	7.9	10.73	3.38	7.35	0.39
Monroe Co.	79	L	7.8	11.98	4.69	7.28	0.43
	80	O	7.5	11.06	4.46	6.60	0.39
	81	F	7.7	9.97	1.71	8.26	0.44

* Hydrogen-ion concentration of the soil at the end of the experiment.

exchangeable calcium found in them. The Volusia silt loam soil from Turkey Hill received the largest application of limestone but it was found to contain considerably less exchangeable calcium than the Volusia silt loam soil from Cayuta. This latter soil, which received a smaller treatment of limestone than did any of the soils, with the exception of those of the Ontario series, contained the largest quantity of exchangeable calcium.

Robinson and Williams (9) found a correlation between the hydrogen-ion concentration of soils collected in North Wales and their content of exchangeable calcium. A similar relationship was found to exist for certain of the soils of Scotland by Ogg and Dow (7). The irrelation of the hydrogen-ion concentration and the magnitude of limestone application to the exchangeable calcium of the soils used in the present study may have arisen from the fact that they differ in their absorptive capacity for calcium when in the presence of calcium carbonate. That is, the alumino-silicic complex of the soils may have reached an equilibrium with respect to the limestone employed in the investigation. When the soils are in this condition, it may be necessary to add excessive amounts of limestone to them before their exchangeable calcium is appreciably increased.

This possibility is reflected when the quantity of exchangeable calcium in the soils of the Ontario series is noted. The addition of limestone to these soils did not change their content of exchangeable calcium. It might be implied that the limestone added to them was not in sufficient quantity to bring about such a change. However, it would seem more likely, since the soils are calcareous, that their absorptive capacity for calcium was in equilibrium with the calcium carbonate which they contained before limestone was applied to them. Below the surface foot they are especially rich in carbonate; calcium carbonate is often present to the extent of 10 per cent. This being the case, it is improbable that larger applications of limestone to the two soils under discussion would have increased, significantly, their adsorption of calcium.

From the results reported by Page and Williams (8) concerning the replaceable calcium in the soil of Broadbalk field, it would appear that this constituent has not changed in quantity, to any considerable extent, in spite of the manurial dressings which the soil received during 82 years. Its colloidal complex may be in a state of equilibrium, as far as calcium is concerned, with respect to the chalk which it contains. On the other hand, Merkle (5) found that a biannual application of lime to a soil for a period of 46 years increased, in large measure, its content of exchangeable calcium. The behavior of this soil, which is reported as containing no carbonate, is similar to that of the soils of the Dutchess and the Volusia series, whereas the behavior of the soil at Rothamsted, which contains chalk, appears to be similar to that of the soils of the Ontario series.

Fertilizers, when applied in addition to limestone, had no noticeable effect on the quantity of exchangeable calcium which was found in the soils from the cylinders. When fertilizers were applied without limestone the exchangeable calcium in each of the first four soils of table 3 is shown to be slightly increased. There is some doubt, however, whether the exchangeable calcium in these soils was actually increased. The calcium sulfate which was contained in the acid phosphate may have increased the quantity of calcium in the alumino-silicic complex of the soils. On the other hand a portion of the calcium shown as exchangeable may have been present in the soils in the form of sulfate. This is of minor importance however, since the increases noted are comparatively

small. The Ontario loam soil from Monroe County is shown to contain more exchangeable calcium when treated with fertilizers alone than when untreated. The reliability of this increase is discredited because the addition of limestone to this soil did not result in a similar effect.

TABLE 4

Relation of total cations to calcium in the diffusates of electrodialyzed soils

(Mgm. equivalents in 100 gm. of air-dry soil)

NUMBER OF CYLINDER	TREATMENT	TOTAL CATIONS IN DIFFUSATE	CALCIUM IN DIFFUSATE
29	F L	12.63	11.52
30	L	10.63	9.75
31	O	1.60	0.65
32	F	1.95	1.20
36	F L	14.69	13.10
37	L	14.55	13.46
38	O	4.49	3.39
39	F	5.50	4.24
43	F L	19.00	18.10
44	L	18.40	17.75
45	O	7.90	6.50
46	F	9.75	8.35
50	F L	14.43	14.10
51	L	14.39	14.18
52	O	2.89	1.80
53	F	3.85	2.50
71	F L	11.15	10.25
72	L	12.35	11.16
73	O	13.45	10.79
74	F	13.30	11.18
78	F L	12.45	10.73
79	L	13.00	11.98
80	O	12.75	11.06
81	F	11.45	9.97

EXCHANGEABLE POTASSIUM

None of the treatments recorded in table 3 was found to influence the quantity of exchangeable potassium in any of the soils when determined by means of electrodialysis. This may have resulted from one of two causes: The concentration of potassium may have been too low to bring about the replacement of other cations or the potassium may have been adsorbed by the soils and subsequently replaced because of the comparative ease with which potassium is recovered from the adsorbing complex of soil (11). Still, Page

and Williams (8) and Merkle (5) have shown that the repeated application of potassium to soils over a period of years resulted in an accession of exchangeable potassium.

TOTAL CATIONS AND CALCIUM IN THE DIFFUSATES OF ELECTRODIALYZED SOILS

The predominant cation in all of the soils studied, irrespective of the treatment which they received, was calcium. From the data presented in table 4 a comparison may be made of the calcium and the total cations contained in the diffusates of the electrodialyzed soils. The total cationic content of each diffusate is shown as slightly more than the corresponding value for calcium. Thus, it is apparent that other exchangeable cations constituted only a small fraction of the total cations of the diffusates.

TABLE 5

The exchangeable calcium and potassium, the hydrogen-ion concentration, and the colloidal content of the untreated soils of the experiment

(Exchangeable calcium and potassium, mgm. equivalents in 100 gm. of air-dry soil)

SOIL	EXCHANGEABLE CALCIUM		EXCHANGEABLE POTASSIUM		H-ION CONCENTRATION		COLLOIDS BEGINNING OF EXPERIMENT
	Beginning of experiment	End of experiment	Beginning of experiment	End of experiment	Beginning of experiment*	End of experiment	
							per cent
Dutchess silt loam, Orange Co	1.80	0.65	0.97	0.61	4.28	4.74	42
Dutchess silt loam, Dutchess Co	5.29	3.39	0.59	0.41	4.84	5.30	42
Volusia silt loam, Cayuta	8.58	6.65	0.62	0.36	4.80	5.29	41
Volusia silt loam, Turkey Hill	4.24	1.80	0.63	0.38	4.98	4.92	40
Ontario loam, Oneida Co	10.61	10.75	0.52	0.48	6.83	6.42	35
Ontario loam, Monroe Co	10.85	6.60	0.59	0.39	6.96	7.50	25

* The hydrogen-ion concentration of the soils at the beginning of the experiment was ascertained from samples which were stored during the course of the experiment.

RELATION OF EXCHANGEABLE CALCIUM IN UNTREATED SOILS TO THEIR COLLOIDAL CONTENT AND HYDROGEN-ION CONCENTRATION

In a preceding paragraph it is stated that certain investigators found a relationship between the quantity of exchangeable calcium in soils and their hydrogen-ion concentration. Although such a relation was not found with respect to the soils of the present investigation after they had been treated with limestone, it was found to exist, to a certain extent, for the same soils when untreated. The hydrogen-ion concentration and the exchangeable calcium of each of the untreated soils, at the beginning and at the end of the 15-year period, are reported in table 5. It may be seen that there is a decided tendency for the soils more alkaline in reaction to contain a larger quantity of

exchangeable calcium than the soils more acid in character. Such a relationship, however, is not suggested when certain of the data of table 5 are considered collectively. It may be observed that, during the 15 years of the experiment, the amount of exchangeable calcium was lowered in all of the soils but one and that the general tendency was for them to become less acid in reaction rather than more acid. The significance to be attached to this latter statement will depend on future research.

There appears to be no relation between the exchangeable calcium in the untreated soils and their colloidal content as estimated by the hydrometer method devised by Bouyoucos (1).

EXCHANGEABLE CALCIUM AND POTASSIUM IN UNTREATED SOILS

It is evident from the results shown in table 5 that, during the period of the experiment, the exchangeable potassium and, with one exception, the exchangeable calcium of the untreated soils was reduced. The exception occurred in the case of the Ontario loam soil from Oneida County, a soil inherently calcareous. Since the soils were subjected to leaching, the extent to which cropping brought about the removal of these cations is not apparent.

Martin (4) found the exchangeable calcium of a number of soils which were relatively high in exchangeable cations to remain constant with prolonged cropping to barley. Under similar conditions he found their content of exchangeable potassium to be reduced. The results of the present study which differ, in the main, from those of Martin with reference to exchangeable calcium may have resulted because of the removal of calcium from the soil in drainage or because of the cropping system employed. It is likely that both of these agencies contributed to the removal of this constituent as well as of potassium.

SUMMARY

Six soils of three different soil series were analyzed for exchangeable calcium and potassium by means of electrodialysis after they were cropped to a 4-year rotation for a period of 15 years. During that time the soils, which were held in iron cylinders, were exposed to natural weather conditions. Each soil type was represented by a series of cylinders. The soils were treated with limestone or mineral fertilizers, or both. The soils of certain cylinders remained untreated.

Limestone was found to increase the exchangeable calcium in some of the soils but not in others. An explanation for this difference in behavior is offered.

A relationship was not found between the quantity of limestone applied to the soils and the quantity of exchangeable calcium which they contained as a result of the treatment. The exchangeable calcium of the untreated soils was found to be related to their hydrogen-ion concentration, but such a relationship did not hold for the soils that were treated with limestone.

Fertilizers when added to the soils with or without limestone had little or no effect on the quantity of exchangeable calcium found in the soils. In no

case did an application of muriate of potash, which was applied with other minerals, enhance the exchangeable potassium of the soils.

At the end of the experiment the soils contained few exchangeable cations other than calcium.

No relationship was found between the colloidal content of the soils and the exchangeable calcium which they contained at the beginning or at the end of the experiment.

During the course of the experiment the exchangeable potassium and, with one exception, the exchangeable calcium of the untreated soils were reduced. In one of the untreated soils the exchangeable calcium remained unchanged.

The results of the experiment suggest that the quantity of exchangeable calcium held in the colloidal complex of humid soils, resulting from an application of calcium carbonate, depends more on the ability of the soils to adsorb calcium than upon the quantity of calcium applied to them in the form of lime. In that event, the hydrogen-ion concentration of a soil that contains native calcium carbonate or one to which lime has been applied would not necessarily be a relative measure of its content of exchangeable calcium.

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SOIL MOISTURE DETERMINATION BY THE ALCOHOL METHOD[1]

ALFRED SMITH AND FRED W. FLINT[2]

University of California

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From time to time, methods have been proposed for soil moisture determinations that would be simpler and more rapid than the oven-drying method. In 1897, Gardner and Briggs (5) suggested an electrical method for determining soil moisture and the following year Gardner (4) reported some modifications and results obtained by this method. Two years later, Briggs (2) reported further improvements in the electrical method. Briggs states that the ordinary method of sampling and determining the loss in weight through drying, when carefully done, is the most accurate method. In order to employ the electrical resistance method for moisture determination, it was found necessary to maintain constant the temperature and amount of salt in solution, or to correct for their variation. Deighton (3) reports that the movement of soluble salts may either vitiate the electrical method or render it too cumbrous for use. Görz (6) has designed an apparatus to determine electrically the soil moisture for ranges from 5 to 25 per cent. Because of the various difficulties in the electrical resistance methods, its use for soil moisture determinations has not been accepted universally.

Bouyoucos has reported on the use of alcohol for the rapid determination of soil moisture. He first used ethyl alcohol but later (1) used methyl alcohol, stating, "It is the most powerful dehydrating agent and is able to replace or reduce the moisture content of soils down to practically the absolutely dry basis." He first air dried his samples, and then oven dried them at 110°C. for 24 hours, cooled them in a desiccator, then added water and determined the amount of the added water that could be recovered by the alcohol method. By this method, he was able to recover 99.01 per cent of the water added to a muck soil, 100.05 per cent in the case of a sand, and practically like quantities from a loam, clay, and silica gel.

METHOD OF PROCEDURE

During the past year we have made several hundred comparisons between this alcohol method and the ordinary oven-drying method (drying to a constant

[1] Paper read before the meeting of the Western Society of Soil Science at Berkeley, California, June 17, 1929.

[2] Associate professor soil technology and associate soil technologist, and graduate student, respectively.

weight at 100°C.). Both ethyl and methyl alcohols have been used and the moisture determined in various types of soil. Moisture tests were made on field soils, on air-dried soils, and on oven-dried soils that were remoistened in the laboratory, as well as on soils leached with distilled water. In all cases samples were run in duplicate both by the alcohol method and by the oven-drying method. The duplicates by the oven-drying method usually agreed more closely. Typical results are herewith reported on the various methods of comparisons used. The hydrometers used were those proposed by Bouyoucos and manufactured by Eimer and Amend and the method was followed in detail.

Results With Yolo Soils

In the first set of samples, soils of the Yolo series were used. These are recent alluvial soils with brown to dark brown surface soil and light brown to brown subsoils, derived from sedimentary and metamorphosed sedimentary rock material. They contain more colloidal material than the usual recent

TABLE 1

Moisture results with field samples of Yolo soils

TEXTURE	MOISTURE		
	Content determined by oven-drying method	Content determined by alcohol method	Recovered by alcohol method
	per cent	*per cent*	*per cent*
Sand	10.61	10.96	103
Fine sandy loam no. 1	20.19	17.86	88
Fine sandy loam no. 2	20.73	17.86	86
Fine sandy loam no. 3	17.30	17.86	103
Clay	27.53	19.96	72

soils in California. The samples used were obtained from the field and represent surface soils. They were well mixed in the laboratory and no additional water was added. Ethyl alcohol was used. The data given in table 1 are averages of two determinations in every case.

In the last column of table 1 the moisture recovered by the alcohol method was determined by dividing the moisture content as found by the alcohol method, by the moisture content as found by the oven-dry method, and multiplying by 100. The data in table 1 are typical of the first group of determinations made. The coarser textured soils gave results by the alcohol method which were in close agreement with those obtained by oven drying to constant weight, but with fine textured soils wide differences occurred, probably because of failure to obtain a complete mixing of the alcohol and moist soil.

Results With Capay Soils

Capay soils have the same origin and mode of formation as the Yolo series, but in age they are classified as "Early Maturity" and have developed under

conditions of restricted drainage. They have subsoil horizons of heavy clay accumulation that are dense and compact. They have brown to dark grayish brown surface soils and brown to grayish brown upper subsoils with yellowish deeper subsoils. The clay members usually have a typical adobe structure. In these determinations ethyl alcohol was used. The data reported in table 2 represent the average of two determinations in each case.

The Capay clay adobe contained black alkali (sodium carbonate) and was taken from a low spot in a pasture. The Capay clay loam contained a fair amount of roots and was obtained from a well-drained spot in a grain field. The heavy members of the Capay series are used in the Sacramento Valley for rice culture, on account of their slow permeability to water. Vigorous stirring for a few minutes failed to disintegrate the Capay soil to any extent, and the alcohol probably did not fully penetrate the moist soil mass.

Time Factor and Amount of Stirring

A Yolo clay soil that had been air dry for 10 years was moistened with distilled water, mixed with the ethyl alcohol, and stirred vigorously for five

TABLE 2

Moisture results with field samples of Capay soils

TEXTURE	MOISTURE		
	Content determined by oven-drying method	Content determined by alcohol method	Recovered by alcohol method
	per cent	*per cent*	*per cent*
Capay clay adobe	34.97	13.24	38
Capay clay loam	10.56	3.46	33

minutes. The amount of moisture indicated was 70 per cent of that determined by the oven-drying method. When this same soil, after being stirred for five minutes, was allowed to stand, covered to prevent evaporation, for varying lengths of time up to 18 hours, the amount of moisture recovered gradually increased to 80 per cent. Similar fine textured soils stirred vigorously for varying periods of time gave a moisture recovery approaching 100 per cent only when the stirring period had been extended to 30 minutes.

Effect of Soluble Salts or Alkali

In irrigated regions, the composition of the irrigation waters in any particular locality may be of decidedly varied character. Kelley (8) has reported the quality of eight irrigation waters whose total soluble salts ranged from 222 to 3,499 p.p.m. Greaves (7) analyzed hundreds of samples of water representing 58 streams, the majority of which are extensively used for irrigation purposes in the Intermountain region. He found that the total salt content varied from 60 to 1,312 p.p.m. The effect of soluble salts on the electrical resistance method for soil moisture determinations has been previously referred to.

As the soil solution is likely to vary in composition throughout the year, and where irrigating water is used the soluble salt content of the soil changes, another variable occurs which might affect the moisture results as obtained by the alcohol hydrometer method. In the alcohol method the value of each gradation on the stem of the hydrometer is determined by mixing the alcohol with a definite quantity of distilled water. In order to test the affect of alkali waters, instead of using distilled water, water containing 5,000 p.p.m. of soluble salts was used to standardize the alcohol float. In this case, the factor obtained was 0.621 cc. of water for each gradation on the stem compared to a factor of 0.710 cc. of water for each gradation when distilled water was used.

The moisture content of coarse textured alkali soils was determined by the two methods, the soil being used in its original condition and also after it had been leached with distilled water. In the original unleached alkali soils where the main ingredient of the alkali was sodium chloride, sodium sulfate, or sodium carbonate, the moisture content by the ethyl alcohol method was 110, 107, and 93 per cent, respectively, of that obtained by the oven-drying method. After these same soils had been leached, the moisture content was 100, 94, and 98 per cent, respectively. Without leaching, the moisture, as determined by the alcohol float method, was likely to be over 100 per cent for the so-called white alkali soils and under 100 per cent for the black alkali (sodium carbonate) soils. After the soils had been leached, however, the moisture recovered was 100 per cent or less for both. The same order of results was obtained when fine textured alkali soils were used.

In order to compare the time required by the operator for the two methods, six different sets of 10 samples each were run by both methods, the time required for the moisture determination of each set being recorded.

The total time required for each sample under the alcohol method includes the time necessary for placing the alcohol in the graduate, for weighing out the soil sample, for mixing the soil with the alcohol, for filtering, for reading the hydrometer and the thermometer, and for cleaning the glassware. It does not include the time required for making the final calculations, as this time is practically the same as that required for calculating results by the oven-drying method.

The total time required for each sample by the oven-drying method includes the time necessary to make the three weighings—empty can, can and moist soil, and can and oven-dry soil. It does not include the time required for cleaning the cans nor does it include the time during which the samples were drying in the oven, as this is not considered as the operator's time.

The soils used in this phase of the work represent three series—the Columbia, the San Joaquin, and the Sacramento. Two sets of 10 samples each were run on each series. The field samples were rather dry and, as previous experience had shown that a greater moisture recovery by the alcohol method was possible when the soil samples were very moist instead of slightly moist, they were wetted with distilled water, thoroughly mixed, and kept in a moisture-saturated

atmosphere for 24 hours before being used for soil moisture determinations. Methyl alcohol was used in this experiment.

The Columbia series is recent alluvial, derived from rock material of mixed origin, light brown to grayish brown surface soil, light brown to brown subsoil, well drained, and has a neutral reaction.

The San Joaquin series is a mature secondary terrace soil, derived from igneous and metamorphosed igneous rocks high in quartz, red to reddish brown surface soil, red to reddish brown upper subsoils, impervious reddish "iron" hardpan and with brown, pervious soil material below the hardpan layer.

TABLE 3

Moisture results with Columbia, San Joaquin, and Sacramento soils by use of methyl alcohol

SOIL SERIES	SETS OF 10 SAMPLES	TOTAL TIME REQUIRED FOR EACH SAMPLE	TIME OF STIRRING FOR EACH SAMPLE	MOISTURE CONTENT		
				Highest	Lowest	Average
		minutes	*minutes*	*per cent*	*per cent*	*per cent*
Columbia sand	No. 1	6	1	12.81	10.74	11.36
Columbia sand	No. 2	5.6	1	11.17	8.93	9.30
San Joaquin fine sandy loam	No. 1	13.8	3	17.99	15.74	16.78
San Joaquin fine sandy loam	No. 2	11.0	3	13.57	13.57	13.57
Sacramento clay	No. 1	15.5	5	41.61	35.23	36.36
Sacramento clay	No. 2	11.5	2.5	33.49	28.45	32.12

TABLE 4

Moisture results with Columbia, San Joaquin, and Sacramento soils by oven-drying method

SOIL SERIES	SETS OF 10 SAMPLES	TOTAL TIME REQUIRED FOR EACH SAMPLE	MOISTURE CONTENT		
			Highest	Lowest	Average
		minutes	*per cent*	*per cent*	*per cent*
Columbia sand	No. 1	1.7	11.73	11.13	11.43
Columbia sand	No. 2	1.7	10.96	10.14	10.46
San Joaquin fine sandy loam	No. 1	2.1	13.58	13.05	13.35
San Joaquin fine sandy loam	No. 2	2.2	13.61	13.07	13.33
Sacramento clay	No. 1	1.6	33.64	31.85	32.84
Sacramento clay	No. 2	1.6	34.40	32.41	33.47

The Sacramento series is a semi-mature secondary lacustrine soil derived from material of mixed origin, dark gray to black surface soil, drab to brown subsoil irregularly calcareous, and with poor drainage.

Table 3 shows the results by the methyl alcohol method.

In table 4, the results obtained by oven drying similar samples of the same series to constant weight at 100°C. are shown.

In making these determinations one operator used the alcohol method while second operator used the oven-drying method, the soil samples being taken at the same time from the original soil, which was kept in a saturated atmosphere.

Therefore, the moisture content as determined by both methods can be compared. This is shown in table 5 using the average moisture content from each set of 10 samples.

The lack of consistency between the two sets from the same soil series, as shown in table 5, may be partially due to a greater quantity of soluble salts in one set than in the other. In mixing soils it is impossible, unless they are extremely moist and have been so for a long period, to obtain a uniform distribution of the soluble salts which are not in solution. The better results obtained with the Sacramento clay soils than with other clay soils previously referred to, are no doubt due to their more mealy condition, for they are high in organic matter, and to the fact that they did not cake up on the stirring rod when mixed with alcohol.

TABLE 5

Comparison of moisture results by methyl alcohol and oven-drying methods on Columbia, San Joaquin, and Sacramento soils

SOIL SERIES	SETS OF 10 SAMPLES	MOISTURE RECOVERED BY ALCOHOL*
		per cent
Columbia sand	No. 1	99
Columbia sand	No. 2	89
San Joaquin fine sandy loam	No. 1	126
San Joaquin fine sandy loam	No. 2	102
Sacramento clay	No. 1	111
Sacramento clay	No. 2	96

* Determined by dividing the moisture content as found by the alcohol method by that found by the oven-dry method and multiplying the quotient by 100.

SUMMARY

Soil moisture determinations made by the usual oven-drying method were compared with those obtained by the alcohol method. Both ethyl and methyl alcohol were used. Some of the soils were used in their natural field condition and others were dried and then either moistened with distilled water or used in the air-dry condition. They represented several soil types and series differing widely in origin, profile characteristics, texture, and organic matter.

With the coarser textured soils, close agreement was usually obtained between the alcohol method and the oven-drying method. In the case of most fine textured soils, the agreement was not close, as it was impossible to obtain a thorough mixing of the alcohol and soil within a few minutes. When the fine textured soils (clays) were vigorously stirred for 30 minutes the results obtained for their moisture content by the two methods agreed closely.

The variation of the composition of the soil solution and amount of alkali salts present affected the accuracy of the alcohol method, the greater density of solution from the alkali soils necessitating a restandardization of the hydrometer.

The actual amount of the operator's time required to determine the soil moisture content by the alcohol method in the case of coarse textured soils was three times as great, and with the fine textured soils five or more times as great, as by the oven-drying method. This does not include the time when the samples were being dried in the oven, as this did not require any of the operator's actual time.

CONCLUSIONS

The oven-drying method is more accurate than the alcohol method but necessitates the delay of 24 hours or more while the soils are in the ovens. The alcohol method gives fairly good results with coarse textured soils, but is unreliable for fine textured soils and those containing alkali. Soil moisture tests can be completed in a short time by the alcohol method but the discordant results with soils of different characteristics make it unsatisfactory for general use.

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THE FIXATION OF THE POTASH OF A GREEN MANURE BY LIMING MATERIALS

W. H. MacINTIRE AND K. B. SANDERS

The University of Tennessee Agricultural Experiment Station

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The turning under of a crop of red clover materially enhances the amount of available potash in a soil system. In many sections of the red clover region of the United States a successful stand of clover requires lime. The influence of liming materials upon the fate of clover-derived potash is therefore of practical importance, as well as of academic interest. Information upon this point was obtained as one phase of a 4-year lysimeter[1] study with 36 tanks that were supplied with water solely by rainfall during the years 1925 to 1928.

EXPERIMENTAL

The tanks were filled May 7, 1925. Each of the $\frac{1}{20,000}$-acre tanks contained 100 pounds of a fairly fertile soil, moisture-free basis, giving a depth of about 8 inches, without subsoil. The brown loam used contained approximately 20 per cent colloids. The soil was obtained nearby and, after being sifted and mixed, was carted under cover to the tanks and protected against drying out during the overnight period required for the determination of its moisture content. The soil was kept fallow throughout the experiment. The annual precipitations for the years of experiment (1925, 1926, 1927, and 1928) were 43.25, 60.67, 44.31, and 70.53 inches, respectively. The rainfall at the end of the fourth annual period was such that the experiment could not be terminated on its fourth birthday, hence 13 months were embraced in this period.

Two tanks were used as no-treatment controls, and two tanks were used for each of the full-depth clover additions of 2 tons and 8 tons, moisture-free basis, without lime. The clover was cut, dried indoors, and powdered in a grinding machine. A homogeneous mixture of leaves and stems was then effected by a thorough mixing with slightly moistened hands. The clover incorporations were made throughout the 8-inch depth of soil, simultaneously with the incorporation of the different liming materials.

Hydrated high-calcic lime, 40–50-mesh and 100-mesh limestone, and dolomite were mixed throughout the soil at one rate only, a constant CaO-equivalence of 2,000 pounds per 2,000,000 pounds of soil. For the 15 duplicate liming additions 30 tanks were required—10 tanks received the liming materials

[1] The installation of the lysimeter equipment was made possible through a grant from W. M. Fulton of Knoxville, Tenn.

only; 10 received lime, plus clover at the 2-ton rate; and 10 received lime, plus clover at the 8-ton rate. The percolates were collected periodically and definite aliquots preserved in acid solution during the accumulation of annual composites. The potassium determinations were made by the chlor-platinate colorimetric procedure.

DISCUSSION

The averaged annual outgo and the total outgo of potassium oxide from each of 18 pairs of tanks are given in table 1. The cumulative losses are shown in figure 1.

Lime-only controls

The outgo of potassium from each pair of tanks that received a liming material alone was less than that from the untreated controls. There was no marked difference, however, between the effects produced upon the native soil potash by the equivalent additions of the several liming materials. The difference between the average potassium oxide outgo from the 10 units of the first group and that from the controls may be considered as determining the repressive effect that the five liming additions uniformly exerted upon the solubility of the native potassic materials. This comparison shows that for the 4-year period the potassium oxide outgo from the unlimed soil was 35 pounds more than that from the limed soil. In every instance, the maximum potassium oxide outgo was obtained during the initial year.

These data are in harmony with those offered in previous contributions (5, 8, 11) which showed that the addition of different calcic and magnesic materials resulted in diminished quantities of potassium salts in the free soil-water of unfertilized soil. Such a diminution has been reflected also in the ash content of such crops as wheat and tobacco (4, 1, 2).

Lipman, Blair, and Prince (3) found that liming diminished the potash content of corn stalks.

Two-ton clover additions

The 2-ton additions of clover supplied 70 pounds of potassium oxide, all of which was water-extractable. The percolates from the clover incorporations without lime showed an enhanced outgo of 39 pounds of potassium oxide, or 56 per cent of the addition, as against a fixation of 32 pounds, or 44 per cent. If the 120-pound outgo of potassium oxide from the lime-only group is compared with the lime-plus-2-ton-clover group, the 24-pound increase in outgo from the 70 pounds of added potash means a recovery of 34 per cent, as against a fixation of 46 pounds, or 68 per cent. As a 4-year average for the five lime-plus-clover treatments, there was a fixation of 25 pounds of potassium oxide from the 35-pound addition supplied by each ton of clover.

The largest outgo of potassium oxide was obtained from the abnormal rainfall of the first year. The second largest outgo came from the subnormal pre-

cipitation during the second year. The heavy rainfall of the final 13-month period leached more potash than did the lighter precipitation of the third year.

Eight-ton clover additions

Table 1 and figure 1 show that the difference between the potassium oxide outgo from the 8-ton clover controls and that from the same additon plus lime is not so great as the corresponding difference obtained in a similar comparison between the 2-ton additions of clover with and without lime. The total potassium oxide outgo from the tanks that received the 280-pound potassium oxide increment carried by the 8-ton unsupplemented additions of clover, amounted to 292 pounds, or an increase of 137 pounds above the outgo from

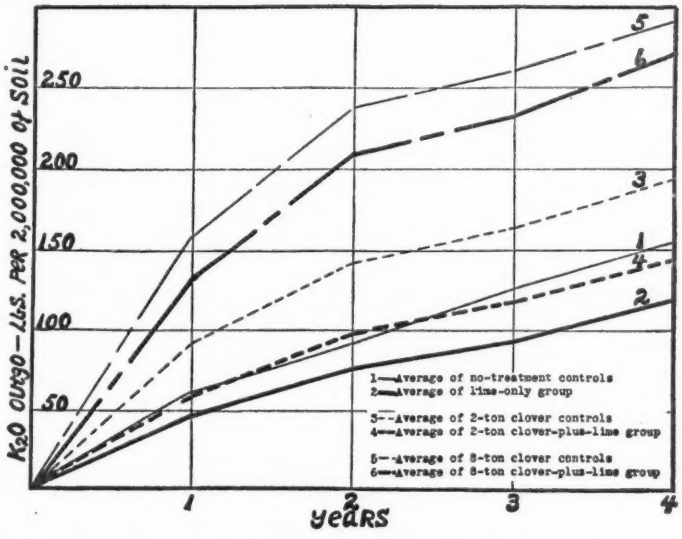

FIG. 1. CUMULATIVE OUTGO OF POTASH FROM LIMED AND UNLIMED SINGLE ADDITIONS OF RED CLOVER OVER A 4-YEAR PERIOD

the untreated soil. This increase is equivalent to 49 per cent of the addition, and shows a fixation of 51 per cent, without the influence of liming materials. The increased outgo of 39 pounds from the 2-ton clover additon thus dropped to an outgo of 33 pounds for each 2-ton fraction of the additional 6 tons that were incorporated in the heavier treatment. Hence, the direct fixation of 39 pounds that was found for the 70-pound potassium oxide addition was increased by 98 pounds, or 47 per cent of the supplemental increment of 210 pounds.

The grand difference between the potassium oxide outgo from the 8-ton clover additions, with and without lime, was only 22 pounds for the 4-year period. Apparently, this is equivalent to a fixation of only 2.75 pounds of

potassium oxide from the 35-pound increment supplied by each ton of clover, as against the fixation of 25 pounds for a ton, which was found in the case of the 2-ton additions.

TABLE 1

Influence of several liming materials upon the outgo of soil potash and that added through additions of green manure, as determined by the composition of rainfall percolates during a 4-year period

TANK NUMBERS	ADDITIONS PER 2,000,000 POUNDS OF SOIL				K_2O LEACHED PER 2,000,000 POUNDS OF SOIL				
	2000-pound CaO ⇔		Green manure		First year	Second year	Third year	Fourth year	4-year total
	Form	Mesh	Weight†	K_2O content					
			pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
301-02	None	...	...	...	59	33	34	29	155
307-8	$Ca(OH)_2$	...	...	...	45	32	20	32	129
309-10	Limestone	100	...	...	46	30	15	27	118
311-12	Limestone	40–50	...	...	48	28	14	25	115
313-14	Dolomite	100	...	...	43	28	20	27	118
315-16	Dolomite	40–50	...	...	54	27	16	23	120
				Av.	47	29	17	27	120
303-4	None	...	4,000	70	92	50	22	30	194
317-18	$Ca(OH)_2$	...	4,000	70	54	45	22	26	147
319-20	Limestone	100	4,000	70	57	44	22	26	149
321-22	Limestone	40–50	4,000	70	65	34	13	25	137
323-24	Dolomite	100	4,000	70	59	42	19	31	151
325-26	Dolomite	40–50	4,000	70	50	42	20	26	138
				Av.	57	41	19	27	144
305-6	None	...	16,000	280	158	80	23	31	292
327-28	$Ca(OH)_2$	...	16,000	280	120	75	23	40	258
329-30	Limestone	100	16,000	280	142	75	25	38	280
331-32	Limestone	40–50	16,000	280	121	64	24	37	246
333-34	Dolomite	100	16,000	280	130	81	26	38	275
335-36	Dolomite	40–50	16,000	280	146	84	22	40	292
				Av.	132	76	24	39	270
Annual rainfall in inches.....					43.25	60.67	44.31	70.53*	218.76

* Thirteen months.

† Moisture-free basis.

The smaller proportionate potash fixation shown for the heavier clover addition with liming materials may have been due to a repressive effect that was induced on the clover controls by the larger quantity of CaO-MgO that was added through the incorporation of the 8-ton manure treatment. The

proportion of potassium oxide and CaO-MgO in the green manure was a constant, of course, for the two rates of clover incorporation. The actual CaO-MgO content of 244 pounds $CaCO_3$-equivalent (CaO 187 pounds, MgO 57 pounds) for the 2-ton clover additions was probably insufficient, however, to enhance materially the fixing power of the unlimed soil. On the other hand, the fourfold increase in amount of clover-derived CaO-MgO (976 pounds, $CaCO_3$-equivalent) may have been sufficient to influence materially the retention of potassium oxide by the soil systems that received the heavier incorporation of green manure without liming materials. The enhancement in CaO-MgO outgo from the 2-ton clover addition during the first year was greater than the CaO-MgO content of the clover. The CaO-MgO content in the percolates from the heavy clover additions, however, was almost exactly double that which passed from the controls during the first year of the experiment, and it was during this period that greatest differences were maintained. The 980-pound $CaCO_3$-equivalent of the CaO-MgO content of the leachings from the non-treatment controls was increased to 1,255 pounds by the 2-ton clover additions and to 1,852 pounds by the 8-ton additions. The enhancements in CaO-MgO outgo for the 244-pound and 976-pound increments supplied by the two clover additions were therefore 275 pounds and 872 pounds, respectively. There was undoubtedly a greater production of carbon dioxide in the tanks that received the heavier clover incorporation, but apparently the enriched carbonated soil-water thus produced was more active toward both native and absorbed calcium oxide and magnesium oxide than toward native or absorbed potassium oxide.

In addition to the foregoing, there was another variable. All of the potash content of the clover was water-soluble. Hence, there was a decided difference in the soil-water concentration of the potassium salts that were derived from the two rates of clover incorporation. With the same, and a sufficient, amount of water available in the soil for the dissolving of all of the potassium oxide carried by the clover additions, the initial concentration of potassium salts furnished by the larger addition was four times that derived from the 2-ton addition. This factor and that of the influence of clover-derived CaO-MgO may both enter into the finding that the fixation of potassium oxide from the 8-ton clover addition with lime appears proportionately less than that from the 2-ton addition plus lime. That is, the difference between the potassium oxide outgo from the 8-ton clover controls and that from the related lime-clover group is not relatively so great as that obtained in a comparison between the 2-ton clover additions, with and without lime.

If the 120-pound average potassium oxide outgo from the lime-only group is used as a basis of comparison against the 270-pound outgo from the group that received lime plus 8 tons of clover, there was an enhancement of 150 pounds in potash outgo, or 37½ pounds for the 70-pound supplement that was derived from each 2-ton portion. This would be equivalent to an outgo of 54 per cent and a fixation of 46 per cent that would be attributable to the effect that was exerted by lime upon the larger addition of potash.

The function of lime in potash fixation

If it be true that all of the added potash entered into the composition of the absorption complex, the depressive action that the several liming materials exerted on potassium oxide outgo might be explained as being a protective effect upon the hydrolysis of the potassium oxide absorption complexes. Related work had shown that, in time, the predominant fractions (7) of the caustic and carbonate additions of calcium and magnesium were fixed or absorbed by the exchange complex. The speed of the absorption of added CaO-MgO was determined by the rapidity of the disintegration of the added carbonates and hence was undoubtedly less rapid than that of the added water-soluble potash. The constant CaO-equivalence of the liming materials was equivalent to only about 10 per cent of the base-saturation coefficient of the soil used. Nevertheless, the percolates were uniformly alkaline. The freshly-formed calcium and magnesium absorption complexes that resulted from the 2,000-pound CaO-equivalent additions were more abundant and more readily hydrolizable than the absorption complexes that were derived from the 280-pound addition of potash. Hence, the outgo of the added potassium was less, and its retention greater, where the liming materials were added.

The foregoing principle would apply, even though the calcium and magnesium bicarbonate content of the free soil-water were enriched by a further concentration of calcium and magnesium in the form of biologically-engendered salts, for it has been shown that the depressive effect exerted by caustic and carbonate forms of calcium and magnesium oxides holds, for native potash at least, even though there should be present an abundance of neutral salts of calcium or magnesium (10). This is equivalent to saying that with this type of soil, and under the prevailing humid conditions, basic interchange and potash liberation do not transpire in the *surface* soil, as a result of economic liming. On the other hand the contrary phenomenon—"reciprocal repression"—is uniformly encountered (10, 6).

It has been pointed out that the decrease in potash solubility, as a result of liming, may be reflected in the ash content of those plants whose feeding powers are limited by their type of root development. On the other hand, it may be that no such effect would be registered by plants of extensive root growth. The availability of the added potash that is made resistant to leaching outgo, as a result of liming, is a problem that calls for supplemental experimentation.

For other types of soil, of smaller colloid content and less retentive power, it may be that the potash retention that is brought about by the several liming materials is a desirable effect and one that would lead to the conservation of fertility.

SUMMARY

Eighteen pairs of $\frac{1}{20,000}$-acre outdoor lysimeters were used to determine the influence that different liming materials exert upon the conservation of clover-derived potash in a fallow soil during a 4-year period. Hydrated high-calcic

lime, 40–50-mesh, and 100-mesh limestone and dolomite were used at a constant CaO-equivalent rate of 2,000 pounds to 2,000,000 pounds of soil. Red clover incorporations were made at the rates of 2 and 8 tons, moisture-free basis.

The results obtained from the control series confirm previous findings to the effect that an economic addition of either of the more commonly used liming materials will produce a diminution in the amount of potash in the free soil-water of an unfertilized soil.

The data show also that the addition of liming materials exerts a marked influence upon the solubility and conservation of the potash that is incorporated through the turning under of red clover. The outgo of potassium oxide is uniformly decreased and the fixation is consequently increased when joint additions of clover-derived potash and lime are made.

The three more commonly used liming materials—hydrated lime, ground limestone, and ground dolomite—seemed to register the same quantitative effect upon potash fixation and outgo.

An explanation was offered of the repressive effect that the several liming materials exerted upon the solubility of the clover-derived potash.

In the case of the 8-ton clover incorporations, it appeared that the CaO-MgO content of the clover was sufficient to enhance the soil's capacity to retain additions of soluble potash.

The largest potassium oxide outgo came from the least rainfall during the first year. The leachings induced by the abnormal rainfall of the second year came next, whereas the excessive precipitation of the fourth year gave potassium oxide leachings in excess of those found for the subnormal precipitation of the third year.

It was pointed out that the availability of the added potash that was rendered less soluble by the liming materials may be specific for plants of different root development and that this phase of the problem requires supplemental study.

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PLATE 1

THE LYSIMETER EQUIPMENT USED IN THE EXPERIMENT

FIG. 1. Exterior view.

FIG. 2. Interior view.

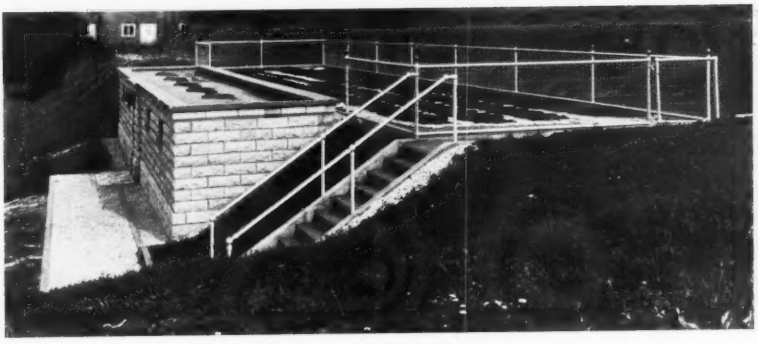

FIG. 1

FIG. 2

AN INDEX OF FRIABILITY OF SOILS

OSWALD CHRISTENSEN[1]

Utah Agricultural Experiment Station[2]

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The term "friability" refers to that characteristic of a material which has to do with the ease of crushing, crumbling, or rubbing apart of the particles of which it is composed. Thus, a loosely compacted sandstone is more friable than a hard limestone or a piece of flint. Likewise, a light, loamy piece of soil is more friable than a heavy, dense piece of clay. Friability is a definite characteristic of a soil and is of special interest to the farmer and to the agricultural engineer.

The behavior of a soil under the plow is given considerable weight by farmers as an index of its capacity for agricultural production. A loose, mellow, loamy sample would, as a rule, be rated as a good soil, whereas a hard, compact, and resistant soil would be regarded as inferior. In conformity with the general definition given, the term "friability" in this paper will be used to designate the composite of all these properties.

Workers in the U. S. Bureau of Soils have supplied tests (1), such as the resistance to penetration by a sharp tool, leading to information as to the friability of the soil. English workers have also investigated the problem with particular reference to cohesion and plasticity (2). In this laboratory, Stauffer has made a study of the tensile strength (4), and various other investigators have made useful contributions in this connection. A precise definition, however, of the term "friability" seems to be lacking, and therefore, of necessity, the literature does not contain definite information as to this important generalized practical soil characteristic. An attempt will be made in this article to describe the construction and operation of a simple testing machine which has been designed to measure this composite characteristic on the basis of a definition to be precisely given in the following discussion. It is not held that the test will measure with precision this general soil character as defined. It is offered rather as a preliminary attempt to measure with

[1] Graduate student. The author gratefully acknowledges the assistance rendered by Dr. Willard Gardner, station physicist, under whose direction the experimental work was done; acknowledgement is also made to Lynn H. Stauffer, a former research assistant in the department of physics, who had previously designed and partly constructed the testing machine described.

[2] Contribution from Department of Physics. Publication authorized by director, July 11, 1929.

precision and with a reasonable amount of effort a character that is very much like that defined.

The fundamental problem of studying this composite character with the view to giving it precise definition and then of measuring it approximately, is essentially similar to that of the engineer's tests for building materials, although the motive of the engineer is to seek materials of adequate strength to resist the necessary stresses, whereas the farmer seeks so to modify his soil as to reduce its resistance to tillage tools of various kinds, i.e., to increase its friability. A good farmer has an intuitive sense enabling him to judge the condition of his soil with fair precision. If the plow furrows lift, crack, and crumble into a mellow loam, the soil is said to be friable, but if they break into clumsy fragments, or if they bend, warp, twist, and turn on edge, leaving a rough upturned mass of corrugations, if the soil is not poor, it is at least in a poor condition. This intuitive method of observation does not furnish numerical facts and figures, and, meritorious as it may be, it is, at least to that extent, admittedly incomplete.

In order that the reader may interpret properly the experimental data presented and at the same time judge as to the appropriateness of designating the compression test selected, as an adequate basis upon which to build the definition of friability, an explanation is given of the terminology and methods used in the study of the strength of materials.

The term "strength" as applied to a piece of building material, like the term "friability" as heretofore only incompletely defined, is obviously ambiguous, but when the adjective "tensile" is prefixed, the ambiguity is at least very much reduced, and if we then add the specification that it refers to a segment of unit cross-sectional area, a number may be assigned for this character to any given specimen, indeterminate only as to the units implied in the measurement of the force and of the area. Most samples of various materials will tend to become deformed to some extent without rupture, so that for each new configuration the sample under test may be assigned an external force that will just neutralize or balance the internal resisting stresses which arise automatically as a result of such deformation. It is clear, however, that as the absolute amount of the deformation will depend upon the size and shape of the sample, it becomes necessary, in order to avoid misunderstanding, to compare the amount of the deformation with the original dimensions, obtaining as the ratio of the two a numerical magnitude called "the unit deformation." If, then, as is usually found to be true of solid materials, the inherent character of the substance predetermines a relationship between the unit stress applied (the stress per unit area) and the unit deformation resulting, it should be possible to establish this relationship experimentally as a characteristic feature of the material. It so happens that for at least a small range of deformation for certain substances the ratio of the unit stress to the unit strain remains practically constant for varying stress, and the configuration reverses itself in consonance with the removal of the applied stress. Such substances are referred

to as elastic and the magnitude of this constant ratio is termed "the modulus of elasticity." On the basis of these stress-strain characteristics, engineers classify most of their materials as either plastic, supple, or elastic. Examples are lead, rubber, steel. Lead tends to flow in response to external stresses with no tendency to reversibility upon removal of the stress; rubber may be very greatly distorted but reverses its configuration on removal of the stress; steel offers great resistance to distortion, reversing upon removal of stress within narrow limits. When the unit stress increases beyond the so-called elastic limit, these elastic materials become permanently deformed, and a point is ultimately reached at which rupture occurs, which is termed the yield point.

For friable materials (and these might be added to the engineering groups as a fourth class of semi-elastic materials) the reversible elastic range is very narrow, and, as the experimental data will show, the magnitude of the unit stress will ascend irreversibly with increasing deformation to a point of maximum stress corresponding to the yield point, as defined, descending again with further increase of deformation in a manner somewhat similar to the stress-strain diagrams furnished by engineers for elastic materials. In the case of soils, however, the yield point corresponds to ultimate rupture, whereas in the case of steel, a readjustment occurs beyond the original yield point, and the unit stress again increases to a higher yield point, which measures the ultimate strength (3). As is evident to students of physics, the area beneath the stress-strain diagram measures the amount of work per unit volume done by the external stress, and, where the curve is a straight line, as is the case to the so-called elastic point, the area up to the elastic limit is equal to one-half the product of the coördinates of this point, and this magnitude is termed "the modulus of elastic resilience." In the case of steel, it represents potential energy. In the case of soils, however, the energy is presumed to represent primarily the work involved in the process of crumbling.

In seeking for an index of friability, an effort is made to measure the ease with which a sample of soil may be crumbled or pulverized. A means of approximating the work of crumbling is provided from the stress-strain diagram, but a measure of the amount of crumbling, if done with precision, is not so readily made. It is proposed, however, in the absence of a more precise method, to make use of the unit deformation as a measure of the crumbling per unit volume. This leads immediately to a precise definition of the index of friability as the ratio of the unit deformation at the yield point to the work of deformation to this point, and for this character the symbol F_m is introduced. As the nature of the stress-strain diagrams for soils will be greatly influenced by the moisture content, it is proposed to introduce a subscript for indicating the moisture content. When the soil is sufficiently moist to flow, i.e., when the high point on the curve tends to vanish, the unit stress remaining practically constant for increasing deformation, or, in other words, when it changes from the friable to the plastic state, the magnitude of the index will become automatically indeterminate.

PRELIMINARY MEASUREMENTS

Much experimental work was done to ascertain the appropriate size of sample. It is evident that, for a compression test, extremes should be avoided in the ratio of the length to the diameter but this preliminary work seemed to indicate that a ratio of approximately 3:2.5 would give consistent and reproducible results. A circular cylinder about 3 cm. long and 2.5 cm. in diameter was therefore chosen for the tests. With such a sample, the buckling effect, on the one hand, and the packing effect, on the other, were reduced to a minimum. Although the crumbling for a compression test is found to be incomplete, inasmuch as the rupture is of a heterogeneous nature, it is a better representative of this composite test than of a tensile or a shearing test.

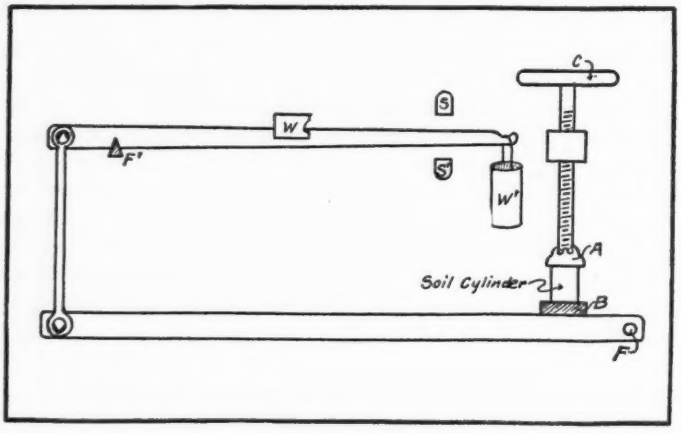

FIG. 1. TESTING MACHINE

APPARATUS

Figure 1 is a sketch of the essential features of the machine used. The heavy framework is not shown. Each of the two lever arms has an advantage of 10 to 1, giving a total advantage of 100 to 1. The sample is placed between the swivel joint plate A and the bearing plate B. The pressure is regulated by sliding W or by adding to W' until the lever leaves stop S and slowly approaches stop S'. This shortens the space between A and B by 0.5 mm. The pressure is recorded, the weights are removed, and the screw crank C is tightened carefully to take up the slack and keep the cylinder under uniform pressure. The test is repeated for the next 0.5 mm. depression, and the process continued until at least ten determinations have been obtained for each sample.

PREPARATION OF SAMPLE

For the experimental work reported in the following, the samples were all ground into a powder. They were then mixed with water, made into a stiff mortar, and molded into small cylinders approximately 2.5 cm. in diameter and 3.1 cm. long. The apparatus used for molding consists of a hollow steel cylinder supplied with an aluminum piston and a threaded cap on the lower

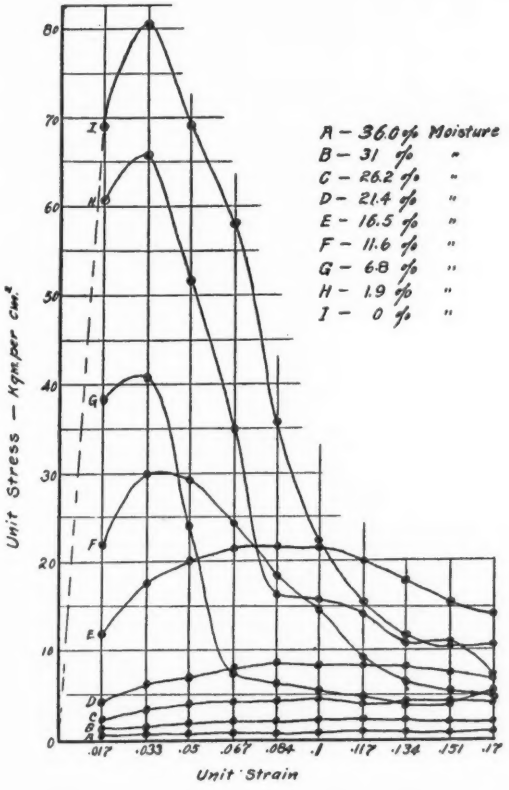

FIG. 2. STRESS-STRAIN DIAGRAM FOR PRESTON RED CLAY

end. By means of the threaded cap and the piston, the length of the cylinder can be regulated. After the soil is pressed into the mold, the cap is removed and the sample forced out by means of the piston. About 30 samples were prepared at a time. After coming from the mold, they were all accurately weighed, and, by the addition or removal of a small portion, brought to the same weight. Three samples were tested in this plastic state and the remainder

placed in a moist dark chamber in order that they might dry slowly and uniformly. With a little experience it was found possible to remove a second set of three from the chamber for test after 1 gm. of water had evaporated, a third set after 2 gm. had evaporated, and so on, until the final tests, which were made after an oven-drying at 100 to 110°C.

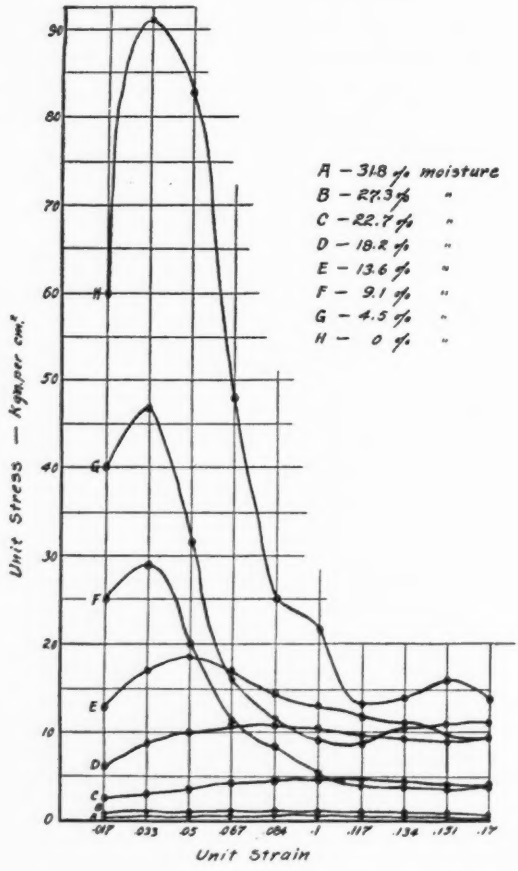

FIG. 3. STRESS-STRAIN DIAGRAM FOR 75 PER CENT CLAY AND 25 PER CENT LOAM

In plate 1, figure 1, are shown four of the samples after being dried. The sample on the left is Greenville loam, from the Central Experiment Farm (Greenville), the one on the right Preston clay, the two intermediate ones representing mixtures of the two soils arranged from left to right in order

of increasing clay. The clay samples had a tendency to crack, as the photograph shows. Such defective samples, however, were discarded and tests made only on samples that showed no tendency to crack.

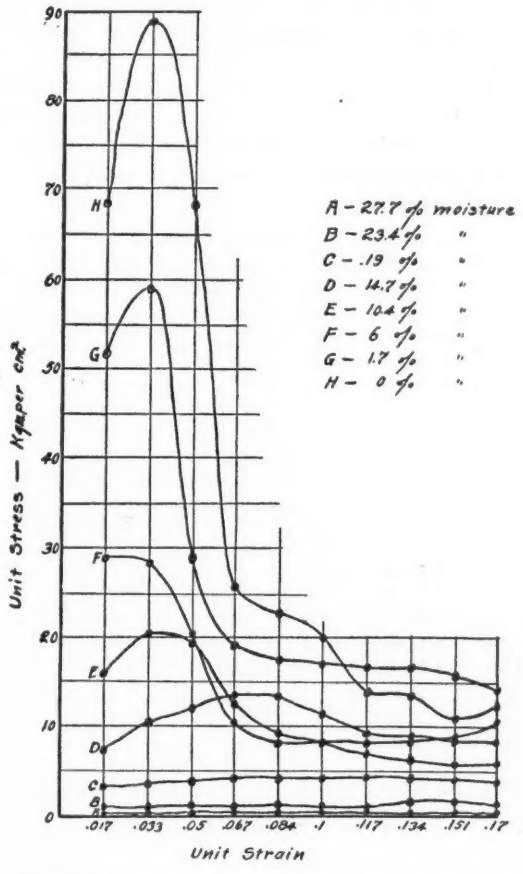

FIG. 4. STRESS-STRAIN DIAGRAM FOR 50 PER CENT CLAY AND 50 PER CENT LOAM

Figure 2 of plate 1 illustrates the manner of rupture; figure 3 shows a heap of fragments of the drier samples as they appear after the test. As is to be expected, from the experience of engineers, they seem to exhibit a rather definite tendency to shear at a 45° angle with the axis of the cylinder (3).

STRESS AND STRAIN RELATION

As previously explained, the compression strength of the soil cylinders was tested for each 0.5-mm. depression. The data are tabulated in table 1, which gives the results of the tests of a mixture of 75 per cent clay and 25 per cent loam. Five additional similar sets of tests with different percentages of clay and loam were thus taken and recorded. The results were reduced to unit stress and unit strain and diagrams plotted (fig. 2 through 6). They reveal the fact that the bearing strength of the damp (plastic) soils remains almost constant as the deformation increases, whereas the extremely dry ones show a distinct increase through a maximum and then down again tending toward the axis, with a gradual transition through the intermediate forms as the moisture content increases.

TABLE 1

Compressive strength in relation to moisture content of a mixture of 75 per cent Preston clay and 25 per cent Greenville loam

Measurements represent an average of three independent tests taken for each 0.5 mm. strain

Length....cm.	3.16	3.12	3.03	2.98	2.92	2.9	2.86	2.83
Diam.....cm.	2.54	2.5	2.43	2.42	2.4	2.36	2.33	2.3
Weight....gm.	29	28	27	26	25	24	23	22
Unit Stress in kgm. per cm.²	1.9±5%	3.2±3%	12±5%	30±11%	60± 8%	111± 3%	170± 7%	253± 6%
	2.0±6%	4.0±5%	15±0%	40± 2%	78±13%	127± 2%	200± 9%	385± 4%
	2.1±4%	4.5±6%	17±4%	47± 4%	83±17%	88± 8%	139±12%	367± 7%
	2.2±7%	4.6±7%	19±3%	50± 5%	75±16%	50±26%	70± 6%	199±21%
	2.4±7%	5.1±6%	20±5%	50± 4%	66±11%	35±34%	51± 8%	107±30%
	2.4±8%	5.5±5%	22±4%	48± 3%	59± 5%	22±54%	40±20%	93±34%
	2.5±7%	5.9±5%	22±4%	45± 4%	55± 7%	20±65%	37±13%	54±60%
	2.6±8%	5.9±5%	21±3%	42± 8%	51± 8%	19±68%	45±13%	59±47%
	2.6±8%	6.1±5%	20±3%	41± 9%	44±11%	19±63%	47± 6%	66±41%
	2.7±8%	6.2±6%	19±8%	43± 7%	41±12%	19±47%	48± 6%	58±43%
Av. P.E.	6.35%	5.3%	3.9%	5.7%	10.8%	37%	10%	29.3%

Grand Average Probable Error = 13.54 per cent.

It is *a priori* evident that the pulverization of a friable material should tend to increase the apparent volume, and the combination of ruptures which begin with the initial stresses is presumed to consist essentially of a pulverization. As the sample shortens more and more beyond the point of rupture or the so-called "yield point," that portion remaining between the plates tends to readhere and pack so that the magnitude of the stress for large deformations tends to become more or less erratic, as the curves indicate.

STRENGTH IN RELATION TO MOISTURE PERCENTAGE AND SOIL COMPOSITION

Figures 7 through 11 give the maximum bearing strength of the samples in the tests described for varying moisture content. The results representing

the mean of three tests seem to follow a definite trend suggesting an exponential law of decrease approaching the horizontal axis asymptotically. The equation,

$$p = p_o e^{-kw} \qquad (A)$$

was therefore used as a basis for smoothing the data. It was first transformed into the logarithmic form,

$$\log p = \log p_o + (\log e^{-k})\, w \qquad (B)$$

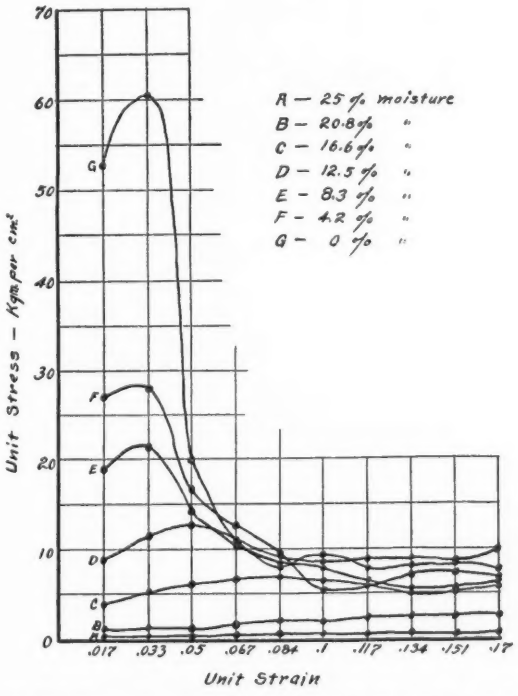

FIG. 5. STRESS-STRAIN DIAGRAM FOR 25 PER CENT CLAY AND 75 PER CENT LOAM

and an auxiliary graph was made of this latter equation, which showed, in some cases, a tendency to break into a pair of straight lines. Inasmuch as the first portion of the curve seems to furnish a better index of friability, because of the packing effect at the other end, this part of the curve was given a little more weight in evaluating the constants. As may be noted, the data fit the curves with fair precision. The constants are assembled in table 2 and the mean error[3] also is shown in each case.

[3] The mean error is the square root of the mean of the sum of the squares of the departures from the curve.

In figure 12 is shown a series of curves, the ordinate representing the unit stress at the yield point and the abscissa the percentage of loam. These soils

TABLE 2

Soil constants for the empirical strength-moisture curves, showing also mean error from formula $\mu = \sqrt{[\epsilon^2]/(n-m)}$

(See "Applicable Mathematics," Silberstein, p. 174)

PERCENTAGE LOAM	P_0	K	μ
0	87	0.1147	5.3
25	91	0.129	2.96
50	79.4	0.146	5.05
75	63	0.143	3.47
100	31.6	0.115	4.95

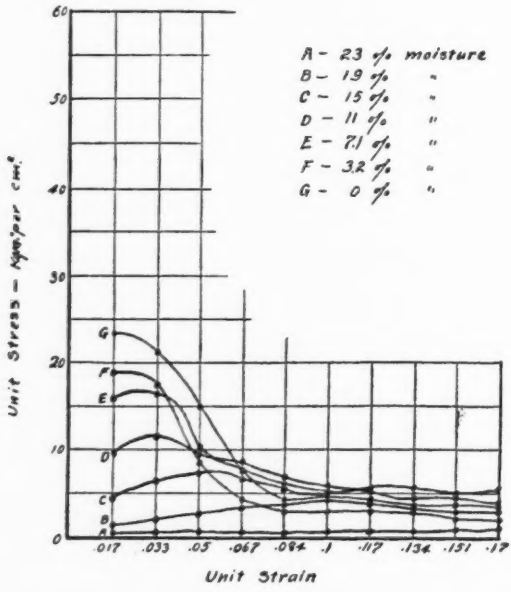

FIG. 6. STRESS-STRAIN DIAGRAM FOR GREENVILLE LOAM

were made up by mixing together two different soils, the one a fine clay, known as Preston clay with Soils Laboratory No. 1669, the other as Greenville loam No. G. The moisture percentage varies from curve to curve as indicated.

THE FRIABILITY INDEX IN RELATION TO SOIL COMPOSITION AND MOISTURE PERCENTAGE

In figure 13 is repeated the information presented in figure 12, transformed in such a way as to show along the ordinate the index of friability as defined, and along the abscissa the soil composition expressed as percentage of loam. In the interest of simplicity, however, in calculating the index of friability, an approximate measure of the work of deformation has been substituted. This

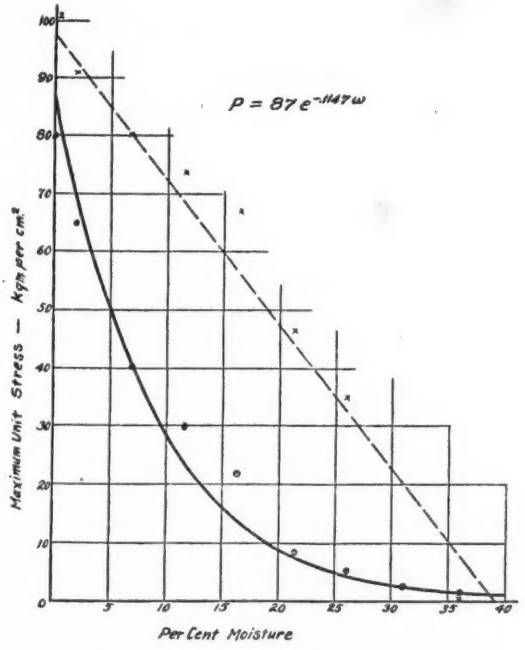

FIG. 7. STRESS-MOISTURE DIAGRAM FOR 100 PER CENT CLAY

has been taken as one-half the product of the coördinates of the yield point on the stress-strain diagram, and the error thus introduced is a measure of the departure of this friable material in its elastic properties from truly elastic materials. Inasmuch as the significance of this error is only of secondary importance when the friability index is construed as an index of comparison of different soils, it is thought advisable to make use of the approximation, at least for this preliminary discussion. The friability index has the dimensions of the reciprocal of a pressure, or force per unit area.

From this approximate definition, and from equation (A),

$$F = F_o e^{kw} \qquad (C)$$

may be written where for $2/p_o$ the symbol F_o is substituted. A knowledge, therefore, of these significant soil constants, F_o and k, enables us to calculate the friability index at any moisture percentage. These constants were taken from table 2 and the theoretical curves of figure 14 were determined. These curves purport to be of preliminary significance only, although over the range

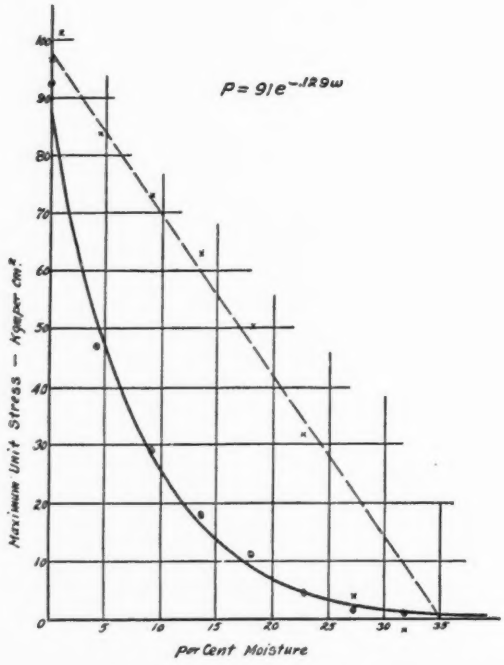

FIG. 8. STRESS-MOISTURE DIAGRAM FOR 75 PER CENT CLAY AND 25 PER CENT LOAM

represented the precision is fair. The probable errors have been determined for one case, as shown in table 1, and the mean error for the one set of empirical curves, as indicated in table 2. The more or less uncertain method of weighting the data, however, in determining the constants of this table, may account for the tendency for the curves of figure 14 to cross. In a general way, however, it is felt that this family of curves furnishes convincing argument in support of the procedure in defining this important soil character, and leads to confidence in the measurements given.

SUMMARY

A study of the mechanical properties of a series of soils indicates that the stress-strain relationships for compression tests are consistent and reproducible.

Data are presented showing the variation of the mechanical characteristics of soils with variation in the composition of the soil and also with varying moisture percentages.

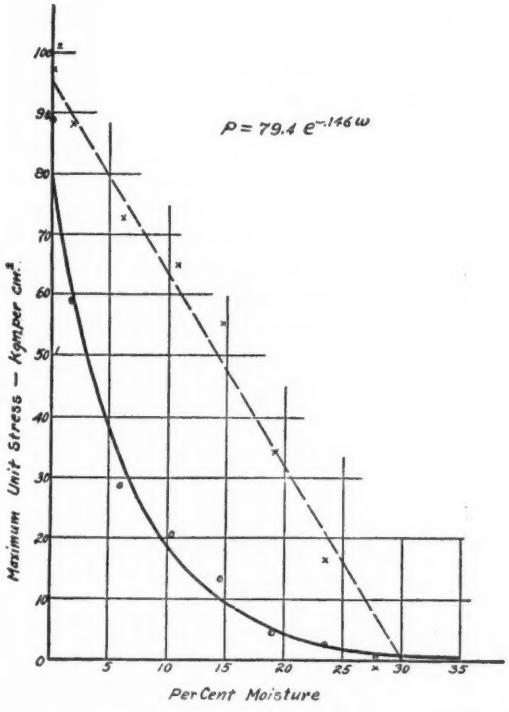

FIG. 9. STRESS-MOISTURE DIAGRAM FOR 50 PER CENT CLAY AND 50 PER CENT LOAM

The property of friability is given a precise definition, and preliminary values are presented. An empirical equation is developed expressing the index of friability F in terms of the moisture percentage w, with two parametric constants characterizing the soil, as follows:

$$F = F_o\, e^{kw}$$

Numerous curves and tables are presented illustrating the development of the theory and the experimental results obtained.

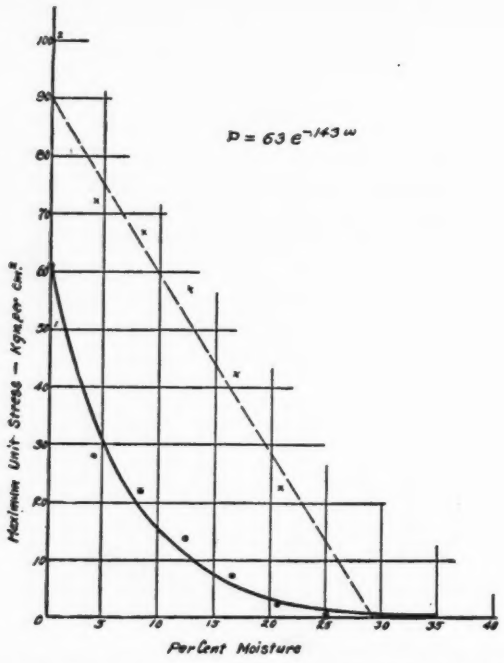

FIG. 10. STRESS-MOISTURE DIAGRAM FOR 25 PER CENT CLAY AND 75 PER CENT LOAM

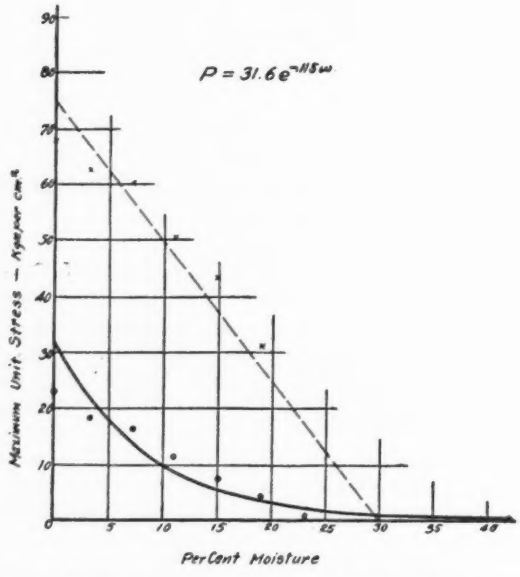

FIG. 11. STRESS-MOISTURE DIAGRAM FOR 100 PER CENT LOAM

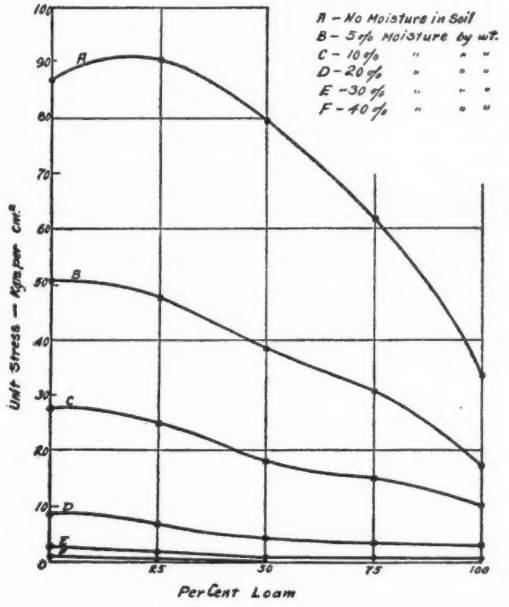

FIG. 12. MAXIMUM COMPRESSIVE STRENGTH OF SOIL OF DIFFERENT MOISTURE CONTENT, IN RELATION TO PERCENTAGE OF CLAY AND LOAM

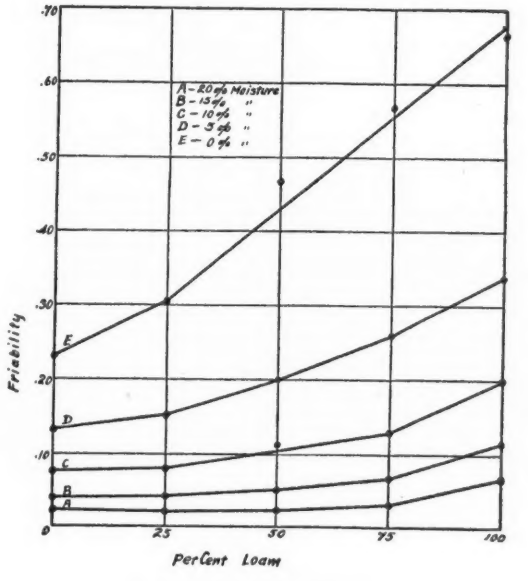

FIG. 13. FRIABILITY DIAGRAM

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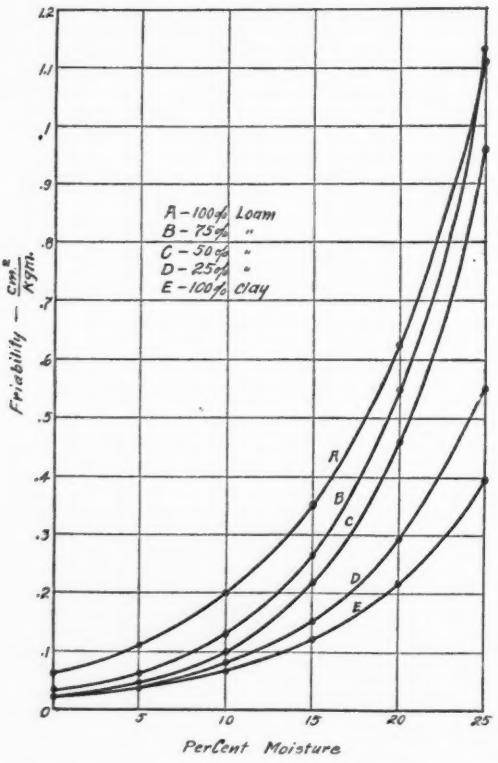

FIG. 14. FRIABILITY AND MOISTURE PERCENTAGE FOR DIFFERENT SOILS

PLATE 1

FIG. 1. Soil samples after being dried. Greenville loam (left), Preston clay (right), Greenville and Preston clay mixtures (center).

FIG. 2. Manner of rupture of samples.

FIG. 3. Fragments of drier samples after test.

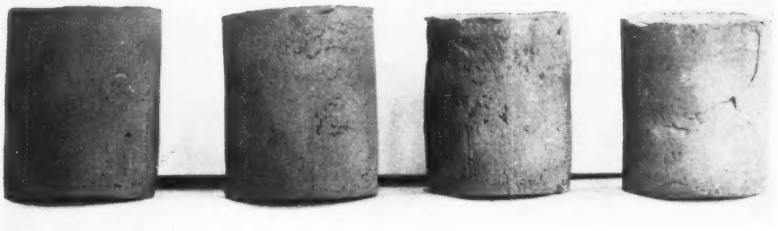

FIG. 1

FIG. 2

FIG. 3

NEUTRALIZING VALUES AND RATES OF REACTION WITH ACID SOILS OF DIFFERENT GRADES AND KINDS OF LIMING MATERIALS[1]

W. H. PIERRE[2]

Alabama Agricultural Experiment Station

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The numerous investigations on the agricultural value of ground limestone of different degrees of fineness have well established the fact that the finer the material the quicker is its action in correcting soil acidity and in promoting plant growth. A thorough review of the subject, however, shows that there is considerable question regarding the value of the coarser grades of materials and that there are few data with regard to the relative values of these materials after varying periods of reaction. This is not surprising when one considers that the methods used in the various investigations have been based on different principles and that those used in the earlier studies have not always been very accurate. Frear (5) in summarizing the work done up to 1921 states:

> Until such results are at hand, it is my conviction from the facts now in hand, that without carrying the detail to extreme refinement, we should duly emphasize the present value of the fine material and avoid all suggestion of considerable and early returns from material coarser than 40 mesh, and certainly from that coarser than 20 mesh.

Since a large amount of the ground limestone on the market contains considerable material coarser than 20 mesh, it seems desirable to obtain as accurate data as possible on the relative rates of reaction and neutralizing values of the materials of different degrees of fineness after different periods of reaction. This seemed especially desirable as a result of some recent investigations by the writer (14), in which the amounts of pure precipitated carbonate required to neutralize the acidity developed through the use of various nitrogenous fertilizers were obtained. From a practical viewpoint it seemed desirable to know what these amounts would be in terms of ordinary limestone or various other liming materials.

It seems desirable also to obtain more quantitative data on the relative rates of reaction and neutralizing powers of the various grades of liming materials if

[1] Contribution from the agronomy department, Alabama Agricultural Experiment Station. Published with the approval of the director.

[2] Associate soil chemist. Since April 1, 1929, Associate agronomist, West Virginia Agricultural Experiment Station. The writer wishes to express his thanks to Joe Bonner, with whom this experiment was started. Because of unavoidable circumstances, Mr. Bonner was unable to continue the work.

it is hoped to make liming recommendations with the idea of bringing soils to definite pH values. That such recommendations seem desirable has been pointed out by Pierre and Worley (16). These investigators proposed certain methods whereby it is possible to determine the amounts of pure precipitated calcium carbonate required to bring soils to definite pH values. In order to be able to make such recommendations on other liming materials, it becomes necessary to have a quantitative measure based on their rates of reaction and neutralizing value as compared with pure precipitated calcium carbonate.

The purposes of this investigation are as follows:

1. To compare the rates of reaction and neutralizing values of various grades and kinds of liming materials when added to soils of different degrees of acidity.
2. To compare the ability of various grades of limestone and liming materials to neutralize the acidity developed in a soil from the use of ammonium sulfate fertilizer.

REVIEW OF LITERATURE

Studies of the relative values of ground limstone of different degrees of fineness have led to two general kinds of recommendations regarding the use of different grades. A number of workers at the various experiment stations have recommended the use of very finely ground material, that is, material most of which passes a 60-mesh or 80-mesh sieve. They believe that the coarse material is too slowly reactive to be of much value in correcting soil acidity. Among these workers who have emphasized the use of finely ground material are: Broughton, et al (4), Haskins and Merrill (8), Thomas and Frear (19), and Patten and Jeffery (13).

The other group has recommended the use of the ordinary ground limestone, that is, material all of which passes a 10-mesh sieve. They believe that if a larger amount of this cheaper material is added there will be enough fine material to become of immediate value and that the coarse material will gradually become available with time. Among such recommendations are those of Bauer and Snider (3), Barker and Collison (2) and White and Garnder (22).

It is not the purpose of this paper to review all the work upon which these recommendations are based. Good reviews have been made by Frear (5), Kopeloff (9), McIntire and Shaw (11), and others. It seems worth while, however, to consider some of the more important investigations briefly. These investigations have usually been based either on one or a combination of more than one of the following methods: (*a*) those based on plant response, (*b*) those based on determinations of the reduction in soil acidity, and (*c*) those based on determinations of undecomposed carbonates.

The first of these methods has been used most generally. Probably the most valuable and comprehensive of such studies are those that were conducted at the Pennsylvania station by White (21), White and Gardner (22), and Thomas and Frear (19). These investigators determined the increased growth of different crops in greenhouse pots when the soil was limed with the various grades of ground limestone. From the data thus obtained they calculated

the relative values of the different grades of limestone, based on a value of 100 for the 100-mesh material, as follows: 69 for the 60-mesh, 22 for the 20-mesh, and 5 for the 8-mesh material.

Kopeloff (9), Hartwell and Damon (7), and Schollenberger (18) made similar studies. In general, their results have shown that the more finely ground the limestone the more effective it is in producing increased crop yields. Considerable variations in the relative values of similar grades of material were obtained, however, by the different investigators or by the same investigator on different soils. Thomas and Frear (19) found that the 20- to 40-mesh material produced on one soil about 55 per cent as much increase in yields as the 100-mesh material, whereas on another soil it produced only about 12 per cent as large increased yields.

Although Kopeloff (9) made no attempt to calculated accurately from his data the relative values of the various grades of limestone used, as measured by plant response, he draws the general conclusion from his study with five different soils that the "200-mesh proved one-third again as effective in influencing crop yields as 20-mesh limestone." If his data are calculated similarly to those of White and Gardner (22), it is found that the relative increases in yields produced by the 20- to 40-mesh material varied from about 21 on a Cumberland silt loam to about 78 on a Portsmouth muck, as compared with values of 100 for the 200-mesh material. The probable reason for such discrepancies will be discussed later in the paper.

With regard to data obtained by means of determinations of the reduction in soil acidity or lime requirement, it is fairly well recognized that many of the methods give only approximate results. Schollenberger (18) states, "In very few instances have the proposed lime requirement methods been considered sufficiently reliable to be of service as indicators of comparatively small changes brought about by the addition of basic material to the soil." This investigator proposed the vacuum lime requirement method and used it in comparing the reaction of various grades of limestone with a Wooster silt loam after periods of contact of 75 and 199 days. In this work 20- to 40-mesh material was compared with material finer than 100 mesh. His results indicate the possibilities of this method.

Measurements of H-ion concentration probably afford the most accurate method of determining the rates of reaction of ground limestone of different degrees of fineness with soils. Recently, Rost and Fieger (17) determined the reduction in H-ion concentration of a number of field soils after they had been limed with different grades and amounts of ground limestone. Since they used different amounts of the coarse grades as well as of the fine grades of material, it is possible to calculate from their data the relative value of the different grades. Their work is valuable from a field point of view and will be discussed further in this paper.

Studies based on determinations of the residual carbonates have given some valuable results. White and Gardner, in the experiments previously men-

tioned, determined the residual carbonates remaining in the soil after three years and found that whereas over 92 per cent of the 100-mesh material had decomposed, only about 46 per cent of the 20- to 40-mesh material had undergone decomposition.

MacIntire and Shaw (11) found that after 4 years the material finer than 40 mesh had undergone practically complete decomposition while only 6½ per cent of the 10- to 20-mesh and 84.9 per cent of the 20- to 40-mesh material had been decomposed.

Ames and Schollenberger (1) made similar studies. They found that after 16 months, 58 per cent of the limestone finer than $\frac{1}{80}$ inch in diameter had decomposed, while only about 23 per cent of the coarse material ranging from $\frac{1}{8}$ to $\frac{1}{20}$ inch had reacted after 23 months. An error may be involved, however, in making such a comparison, since the amounts of lime added were apparently higher than were needed to correct the acidity of the soil.

DETERMINING THE RELATIVE VALUE OF DIFFERENT GRADES OF LIMING MATERIALS

Some of the important factors to be considered in determining the relative values of different grades of liming materials are as follows:

1. The amounts of liming materials added as related to the amounts required to neutralize the acidity of the soil or that required to give maximum growth of the crops used in the study.
2. The acidity of the soil especially as regards its intensity or H-ion concentration.
3. The time allowed for the reaction between the soil and liming material.
4. The downward movement of lime and the question of soil heterogeneity when the studies are made with field plots.

The first of these factors has often been overlooked in the investigations based on plant response or increases in crop yields. Although the effect of different grades of liming materials on crop yields would seem to be the final test, it can readily be seen that if only one uniform rate of the various materials is used, erroneous conclusions are likely to be drawn unless a careful consideration is given to the amount of lime required to give optimum yields of the particular test crop on the particular soil studied. This point can be readily illustrated. It is evident, for example, that if maximum yields can be secured by the addition of one ton of finely ground calcium carbonate, and two tons are added as the standard of comparison, the coarser grade material used at a similar rate will give high and erroneous values. Thus, it may be assumed for sake of illustration that 25 per cent, or 1,000 pounds, of the coarse material added becomes reactive during the progress of the experiment. Then, if only 2,000 pounds of the 4,000 pounds of fine material added are effective in producing increased crop yields, the erroneous conclusion would be drawn that the coarse grade material was 50 per cent as effective as the fine material. This, no doubt, partly explains the different values obtained for similar grades of material by Frear (5), White and Gardner (22), and Kopeloff (9), as previously referred to.

In experiment III of this paper the importance of this consideration is further illustrated.

When excessively large amounts of the liming materials are used another effect may be involved, that is, the possibility of injury to crop growth from overliming. Leichte (10) and Kopeloff (9) in some of their experiments, obtained smaller yields from the use of fine material than from the use of coarser material. The explanation of their results, no doubt, lies in the fact that such large amounts of liming materials were used as to result in lime injury in the case of the highly reactive, finely ground material.

On the other hand, if the amounts of the various grades of limestone added are small as compared with the actual needs, the coarse grade material may show no immediate value, because it has changed the reaction of the soil so slightly as not to be effective. The results obtained by Griffith (6) and others may be due to this cause. Griffith reported that the grasslands of Wales did not respond to any appreciable extent to ground limestone which could not pass a no. 100 sieve, whereas the finest grades of materials were very effective.

The acidity of the soil with respect to the rate of decomposition of various grades of liming material is also an important consideration. It seems very probable that the coarse particles of limestone would react more quickly when added to a very acid soil than when added to a slightly acid soil or to one that is neutral. This factor has been studied in the experiments reported in this paper.

The time factor is also an important consideration. It is evident that although the coarse material may be slowly reactive, as has been shown by various investigators, yet if it is reactive in a reasonable length of time its value cannot be overlooked.

Most of the experiments reported on the problem of fineness of division of limestone have been done with soils in pots. Although this method is open to the objection that it may not represent field conditions accurately, it overcomes some of the difficulties involved in field plots. These factors are: the depth at which the lime reacts; the difficulty of getting a thorough mixture of the coarse grade materials with the soil, especially if used in small amounts; and the question of soil heterogeneity. Careful consideration of these factors in field studies would be required.

PROCEDURE

This investigation consists of three experiments which are very similar in purpose but which, for convenience, will be discussed separately. Experiment I consists of a study of the rates of reaction of various grades of limestone and basic slag with two medium acid soils. Experiment II consists of a similar study except that the soils used were more acid and that more kinds of liming materials were studied. Experiment III is a study of the ability of various grades of limestone, basic slag, and crushed oyster shells to correct the acidity developed by ammonium sulfate fertilizer.

These investigations were conducted in pots in the greenhouse. One-gallon pots containing 4,000 gm. of soil were used in experiments I and II, and 2-gallon pots containing 8,000 gm. of soil were used in experiment III.

The liming materials used in the experiments were as follows: precipitated calcium carbonate (C.P.); ground limestone, including unassorted, coarser than 20 mesh, 20 to 60 mesh, 60 to 100 mesh, finer than 100 mesh; crushed oyster shell of the same grades as used for ground limestone; regular basic slag (18 per cent P_2O_5); low-grade basic slag (11 per cent P_2O_5), including unassorted (all passes through 8-mesh sieve), coarser than 20 mesh, 20 to 60 mesh; marble dust (all passes through 100-mesh sieve).

TABLE 1

Mechanical and chemical composition of the liming materials used in this study

LIMING MATERIAL	FINENESS OF MATERIAL	PERCENTAGE FOUND IN UNASSORTED SAMPLE	CALCIUM CARBONATE EQUIVALENT
			per cent
Ground limestone	Unassorted	100	82.2
	Coarser than 20 mesh	29.9	84.9
	20 to 60 mesh	31.8	81.7
	60 to 100 mesh	14.2	80.2
	Finer than 100 mesh	24.1	80.0
Crushed oyster shell	Coarser than 20 mesh	3.9	98.8
	20 to 60 mesh	42.6	92.4
	60 to 100 mesh	18.4	89.2
	Finer than 100 mesh	35.2	86.2
Basic slag (regular)	Unassorted	100	70.6
Basic slag (low grade)	Unassorted	100	76.0
	Coarser than 20 mesh	8.6	63.7
	20 to 60 mesh	20.1	72.4

The mechanical analysis of the materials and their neutralizing value toward boiling 0.4 *N* HCl are given in table 1.

The liming materials were thoroughly mixed with the soil at the beginning of the experiment. No plants were grown in the pots except in those of experiment III. The soil in the pots was brought to about optimum moisture content and the pots were kept in the greenhouse throughout the experiment. The greenhouse was unheated during the winters, but at no time did the soils freeze. From time to time rain water was added to replace that lost by evaporation. The soils were allowed to become fairly dry, however, before they were brought back to optimum moisture. This seemed desirable in order to simulate field conditions as much as possible.

Samples of soil were removed from the pots at intervals. The soil was always allowed to dry in the pot to some extent before it was emptied into a pan,

thoroughly mixed, and the sample taken. After removal of the sample, the bulk of the soil was returned to the pots, and water was added to bring it back to approximate optimum moisture content.

By means of the "dialysis-colorimetric" method (15), determinations of H-ion concentration were made on the samples soon after they were taken. By comparing the H-ion concentration of the soils treated with the various liming materials with that of the soils treated with varying amounts of precipitated calcium carbonate, it was possible to determine the relative rates of reaction and neutralizing powers of the various materials after different periods of time.

TABLE 2

H-ion concentration of a Norfolk sandy loam after various periods of reaction with different kinds and grades of liming material in greenhouse pots

LIMING MATERIALS				H-ION CONCENTRATION OF SOILS AFTER VARIOUS PERIODS						
Kind	Grade	Amount to the acre		½ month	1½ months	4 months	6 months	13 months	16 months	24 months
		Actual	Equiv. pure $CaCO_3$							
		pounds	*pounds*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
Check	...	...	...	5.70	5.70	5.65	5.65	5.60	5.45	5.38
Precipitated $CaCO_3$	...	400	400	6.00	6.00	5.80	5.75	5.65	5.60	5.45
Precipitated $CaCO_3$	...	800	800	6.40	6.15	6.20	6.00	6.00	5.95	5.85
Precipitated $CaCO_3$	...	1,500	1,500	6.85	6.60	6.40	6.45	6.40	6.38	6.08
Precipitated $CaCO_3$	...	2,000	2,000	7.05	6.75	6.70	6.70	6.60	6.50	6.43
Ground limestone	Unassorted	2,000	1,645	6.15	6.10	6.20	6.10	6.05	6.15	6.05
Ground limestone	Coarser than 20 mesh	2,000	1,700	5.70	5.70	5.75	5.70	5.65	5.60	5.50
Ground limestone	20 to 60 mesh	2,000	1,635	5.80	5.80	6.00	6.05	6.20	6.05	5.93
Ground limestone	60 to 100 mesh	2,000	1,605	6.10	6.20	6.30	6.45	6.60	6.45	6.30
Ground limestone	Finer than 100 mesh	2,000	1,600	6.65	6.60	6.65	6.50	6.45	6.40	6.25
Regular basic slag	Unassorted	3,000	2,420	6.60	6.55	6.45	6.55	6.40	6.55	6.40
Low grade basic slag	Unassorted	3,000	2,580	6.35	6.30	6.40	6.40	6.40	6.28	6.10

The detailed procedure used in experiment III will be given in the discussion of that experiment.

EXPERIMENTAL DATA

Experiment I

This experiment was started in February, 1927. The two soils used were different in origin and in texture and were medium acid. Precipitated calcium carbonate was used as the standard of comparison and used at four different rates with each soil; the highest rate used was calculated to give a pH value of 7.0. The ground limestone additions were made at a rate similar to the highest rate of precipitated calcium carbonate, but because the limestone was not pure

the actual calcium carbonate applied was only about three-fourths this amount.

The amounts of material added and the average of duplicate determinations of the H-ion concentration of the soils obtained after different periods of reaction are given in tables 2 and 3. In studying the data, the increases in the H-ion concentration of the untreated samples during the progress of the experiment must be considered, for whatever factors caused this increase must also have been active in the case of the limed soils. It will be seen, for example, that although the H-ion concentration of the soils treated with the readily reactive precipitated calcium carbonate increased after the first four months, the differ-

TABLE 3

H-ion concentration of a Decatur silt loam after various periods of reaction with different kinds and grades of liming materials in greenhouse pots

LIMING MATERIALS				H-ION CONCENTRATION OF SOILS AFTER						
Kind	Grade	Amount to the acre								
		Actual	Equiv. pure $CaCO_3$	½ month	1½ months	4 months	6 months	13 months	16 months	24 months
		pounds	*pounds*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
Check	...	...	...	5.55	5.50	5.60	5.60	5.40	5.40	5.20
Precipitated $CaCO_3$	...	1,000	1,000	6.10	6.05	6.05	6.00	5.80	5.65	5.65
Precipitated $CaCO_3$	...	2,000	2,000	6.40	6.15	6.25	6.10	5.95	5.85	5.85
Precipitated $CaCO_3$	...	4,000	4,000	7.05	6.80	6.80	6.60	6.60	6.45	6.43
Precipitated $CaCO_3$	...	5,000	5,000	7.40	7.00	6.95	6.70	6.80	6.70	6.68
Ground limestone	Unassorted	5,000	4,110	6.00	6.05	6.10	6.15	6.00	6.00	6.08
Ground limestone	Coarser than 20 mesh	5,000	4,245	5.60	5.60	5.65	5.70	5.60	5.45	5.50
Ground limestone	20 to 60 mesh	5,000	4,085	5.65	5.70	5.85	6.05	6.05	5.85	5.93
Ground limestone	60 to 100 mesh	5,000	4,010	6.00	6.20	6.40	6.65	6.65	6.60	6.50
Ground limestone	Finer than 100 mesh	5,000	4,000	6.75	6.70	6.70	6.60	6.55	6.55	6.50
Regular basic slag	Unassorted	7,500	5,295	6.65	6.60	6.60	6.65	6.70	6.60	6.53
Low grade basic slag	Unassorted	7,500	5,700	6.35	6.45	6.40	6.60	6.60	6.45	6.43

ence between their pH values and those of the untreated soil did not change materially.

The results obtained with the two soils are quite similar. In order to study these data more carefully and to evaluate the different grades of limestone and basic slag in terms of pure calcium carbonate, graphs were drawn and calculations made therefrom. The amounts of pure calcium carbonate added to each soil were plotted against the resulting H-ion concentration of the soil. A graph was thus made from the data obtained after each interval of time and for each soil. From the graph was determined the amount of pure precipitated calcium carbonate required to bring the soil to the same pH value as was obtained by the use of various liming materials. The relative values of the materials,

based on a value of 100 for pure calcium carbonate, were thus obtained and are given in table 4. It must be remembered that the pH values upon which these data are based may be subject to an error of 0.05 pH and possibly, in some cases, of 0.10 pH and that these small differences may cause a large percentage error where the amounts of material reacting are small. The value obtained

TABLE 4

Relative neutralizing values of various kinds and grades of liming materials after various periods of reaction with medium acid soils

LIMING MATERIAL	SOIL	RELATIVE VALUES, BASED ON PRECIPITATED $CaCO_3$ AS 100, AFTER VARIOUS PERIODS OF CONTACT						
		½ month	1½ months	4 months	6 months	13 months	16 months	24 months
Ground limestone (unassorted)	Norfolk S. L.	34	40	49	58	55	69	87
	Decatur T. L.	20	24	30	54	52	61	68
	Average	27	32	40	56	54	65	78
Ground limestone (coarser than 20 mesh)	Norfolk S. L.	0	0	16	15	23	23	26
	Decatur T. L.	2	5	2	6	12	5	16
	Average	1	3	9	11	18	14	21
Ground limestone (20 to 60 mesh)	Norfolk S. L.	8	9	37	54	72	58	63
	Decatur T. L.	5	10	13	37	56	49	56
	Average	7	10	25	46	64	54	60
Ground limestone (60 to 100 mesh)	Norfolk S. L.	31	55	75	108	125	114	114
	Decatur T. L.	20	54	63	113	106	115	107
	Average	26	55	69	111	116	115	111
Ground limestone (finer than 100 mesh)	Norfolk S. L.	76	94	120	100	102	94	109
	Decatur T. L.	76	93	90	100	96	110	108
	Average	76	94	105	100	99	102	109
Regular basic slag	Norfolk S. L.	49	59	65	71	63	88	81
	Decatur T. L.	52	64	62	89	85	87	83
	Average	51	62	64	80	74	88	82
Low grade basic slag	Norfolk S. L.	29	40	58	55	58	52	60
	Decatur T. L.	32	51	44	70	70	70	70
	Average	31	46	51	63	64	61	65

from the average of the two soils, however, should give a fairly accurate value for the different grades of materials after varying intervals of time.

It will be noted that the relative value of the unassorted limestone as compared with that of pure calcium carbonate has increased from 27, after 1½ months, to 78, after 2 years. This gradual reaction, with time, of the materials containing coarse particles is seen in all cases. The finely divided materials, that is the limestone ground finer than 100 mesh, reacted nearly as rapidly with the soil as did the pure, precipitated calcium carbonate.

The coarse grade limestone seems to have reacted slightly more rapidly with the Norfolk sandy loam than with the Decatur silt loam. If the average values are considered, it will be seen that the material that does not pass through a 20-mesh sieve is very slow in reaction and gives a relative value of only 20 after 2 years, as compared with pure calcium carbonate. After this same period of time the relative values for the other grades of materials were as follows: 78 for the unassorted limestone, 60 for the 20 to 60 mesh, and over 100 for the limestone material finer than 60 mesh. The reason for the latter materials giving values of over 100 may be partly explained by the experimental error and partly by the following consideration. From these and other investigations it seems probable that there is a slight tendency of limed soils to increase slightly in H-ion concentration after the carbonates have been decomposed. Since the highly reactive precipitated carbonate, used as the standard of comparison, would be decomposed most quickly, the soils treated with it would show this tendency to increased H-ion concentration first. This fact would help to explain the high values for the finely ground limestone mentioned, since the standard of comparison is precipitated calcium carbonate.

If the results from basic slag are next considered, it will be seen that about one-half of the total neutralizing action of the regular slag is effective within 15 days after application, and that after 2 years about four-fifths is effective. The low grade slag, as will be seen, is less readily reactive, no doubt because it contains more coarse material.

Experiment II

One of the factors that was believed to influence the rate of decomposition of the various grades of limestone is the acidity of the soil. If the soil is very acid it would seem that the materials would be decomposed more quickly. This experiment was started with the purpose of studying the rates of reaction of various liming materials applied at two different rates to very acid soils. The Cecil sandy loam was taken from the ammonium sulfate plot of the old source-of-nitrogen-experiment at Auburn, Alabama, and had a pH value of 4.65. The Susquehanna clay is a subsoil of an extremely high acidity. Tidmore and Parker (20) found the avidity of the acids in this soil to be very high. Additional liming materials to those used in experiment I were added to this experiment.

The soils were limed in November, 1927. Two different rates of the various materials were used with the Cecil sandy loam, one rate calculated to bring the soil to pH 6.0, and the other to pH 7.0. Since some of the liming materials were not pure, however, these values were not always obtained even with the finely ground material. An application of 10 tons an acre was used with the Susquehanna clay.

The data from the Cecil sandy loam are given in table 5. By graphs and the same method of calculation as was used in experiment I, the comparative values of the liming materials after various periods of time were obtained

(table 6). It will be noted that there is no consistent difference between the relative values obtained from the coarse grade materials when applied in small amounts and in large amounts. If differences actually exist they seem to be

TABLE 5

H-ion concentration of a very acid Cecil sandy loam after various periods of contact with different kinds and amounts of liming materials in greenhouse pots

LIMING MATERIALS				H-ION CONCENTRATION OF SOILS AFTER			
Kind	Grade	Amount to the acre		1 month	3 months	6 months	12 months
		Actual	Equiv. pure $CaCO_3$				
		pounds	*pounds*	*pH*	*pH*	*pH*	*pH*
Low amounts of materials							
Check	...	...	...	4.65	4.65	4.65	4.63
Precipitated $CaCO_3$	...	750	750	5.00	5.25	5.33	5.15
Precipitated $CaCO_3$	...	1,500	1,500	5.80	5.75	5.63	5.65
Precipitated $CaCO_3$	...	2,325	2,325	6.25	6.30	6.03	5.93
Ground limestone	Coarser than 20 mesh	2,325	1,975	4.70	4.80	4.88	4.88
Ground limestone	20 to 60 mesh	2,325	1,900	4.95	5.75	5.65	5.63
Ground limestone	60 to 100 mesh	2,325	1,865	5.60	5.95	5.75	5.65
Ground limestone	Finer than 100 mesh	2,325	1,860	5.95	5.90	5.75	5.83
Marble dust	Finer than 100 mesh	2,325	2,325	6.00	6.15	5.98	5.95
Crushed oyster shell	Coarser than 20 mesh	2,325	2,300	4.65	4.60	4.83	5.68
Crushed oyster shell	20 to 60 mesh	2,325	2,150	4.80	5.90	5.88	5.65
Crushed oyster shell	60 to 100 mesh	2,325	2,075	5.80	6.10	5.88	5.93
Crushed oyster shell	Finer than 100 mesh	2,325	2,005	6.05	6.05	5.95	5.98
Regular basic slag	Unassorted	2,325	1,640	5.45	5.40	5.50	5.45
Low grade basic slag	Coarser than 20 mesh	2,325	1,480	4.75	4.75	4.85	4.85
Low grade basic slag	20 to 60 mesh	2,325	1,685	5.00	5.25	5.18	5.23
High amounts of materials							
Precipitated $CaCO_3$	...	3,000	3,000	6.75	6.40	6.43	6.18
Precipitated $CaCO_3$	...	5,250	5,250	7.35	7.30	7.08	7.18
Ground limestone	Coarser than 20 mesh	5,250	4,460	4.80	5.25	5.38	5.13
Ground limestone	20 to 60 mesh	5,250	4,290	5.60	6.45	6.33	6.15
Ground limestone	60 to 100 mesh	5,250	4,210	6.40	6.90	6.68	6.65
Ground limestone	Finer than 100 mesh	5,250	4,200	6.80	6.95	6.75	6.68
Marble dust	Finer than 100 mesh	5,250	5,250	6.60	6.90	6.88	6.95
Crushed oyster shell	Coarser than 20 mesh	5,250	5,190	4.60	4.95	5.30	5.18
Crushed oyster shell	20 to 60 mesh	5,250	4,850	6.00	6.45	6.50	6.65
Crushed oyster shell	60 to 100 mesh	5,250	4,685	6.60	7.00	6.85	6.55
Crushed oyster shell	Finer than 100 mesh	5,250	4,525	7.00	7.05	6.95	6.95
Regular basic slag	Unassorted	5,250	3,705	5.95	6.20	6.18	6.03
Low grade basic slag	Coarser than 20 mesh	5,250	3,345	4.80	4.95	5.28	5.10
Low grade basic slag	20 to 60 mesh	5,250	3,800	5.00	5.65	5.78	5.88

within the limit of experimental error. The average values obtained from the two rates of application will, therefore, be considered.

If the data presented in this table are compared with those obtained with

TABLE 6

Relative values of various kinds and grades of liming materials after various periods of reaction with an acid Cecil sandy loam

LIMING MATERIALS			RELATIVE VALUES BASED ON PRECIPITATED $CaCO_3$ AS 100, AFTER PERIODS OF							
			1 month		3 months		6 months		12 months	
Kind	Grade	Amounts	Per treatment	Average	Per treatment	Average	Per treatment	Average	Per treatment	Average
Ground limestone	Coarser than 20 mesh	Low	7	7	9	13	13	17	19	18
		High	7		17		20		16	
Ground limestone	20 to 60 mesh	Low	36	34	79	76	83	75	78	73
		High	31		72		66		68	
Ground limestone	60 to 100 mesh	Low	71	66	96	99	97	95	80	88
		High	61		101		93		96	
Ground limestone	Finer than 100 mesh	Low	95	86	94	100	97	98	109	104
		High	77		105		98		99	
Crushed oyster shell	Coarser than 20 mesh	Low	0	0	0	4	9	12	...	16
		High	0		7		14		16	
Crushed oyster shell	20 to 60 mesh	Low	16	23	80	72	94	81	70	77
		High	30		64		68		84	
Crushed oyster shell	60 to 100 mesh	Low	72	66	98	97	97	97	112	97
		High	59		96		96		82	
Crushed oyster shell	Finer than 100 mesh	Low	98	99	98	101	109	107	113	109
		High	99		103		105		105	
Marble dust	Finer than 100 mesh	Low	81	67	90	86	97	93	103	97
		High	53		81		88		91	
Regular basic slag	Unassorted	Low	73	61	59	59	73	72	73	72
		High	48		59		71		71	
Low grade basic slag	Coarser than 20 mesh	Low	15	13	9	10	15	19	21	21
		High	10		11		22		20	
Low grade basic slag	20 to 60 mesh	Low	44	32	44	40	36	43	52	55
		High	20		36		49		57	

the medium acid soils given in table 4, it will be seen that the reaction has been more rapid. This is especially noticeable in the 20- to 60-mesh ground limestone. After 1½ months, the average value of this material with the medium acid Norfolk and Decatur soils was about 10 and the value with the very acid Cecil sandy loam was 34 after an even shorter period of time. Similarly, the respective values after 6 months were 46 and 75. If the other grades of limestone are similarly compared, a greater rate of reaction is also noted with this very acid soil than with the medium acid soils of experiment I.

A comparison of the values obtained for ground limestone and crushed oyster shells of similar degrees of fineness indicates that there is very little difference between these two sources of materials except in the case of the materials coarser than 20 mesh. It would seem that this grade of material is more readily available in the form of ground limestone than in the form of crushed oyster shell.

The coarser grades of basic slag are seen to have a much lower neutralizing value than the regular slag, made up nearly entirely of fine material. The slag coarser than 20 mesh has about the same value as the corresponding size of material in ground limestone.

Marble dust, because of its extremely fine state of division, largely reacted during the first three months.

Tables 7 and 8 give the data obtained with the Susquehanna clay. The intense acidity of the soil is seen from these data, for even with an application of 10 tons of precipitated calcium carbonate an acre, the reaction after 1 year is only pH 5.43. It will be noted from the data given in table 8 that the rates of decomposition, especially of the coarser grades of limestone, are even faster in this soil than in the acid Cecil sandy loam soil, and considerably faster than in the two medium acid soils used in experiment I. Whereas the relative value after 1 year for ground limestone coarser than 20 mesh was found to be 18 with the Cecil soil, it was found to be 37 with the Susquehanna clay. It must be remembered, in this connection, that the clay has an intensity of acidity very seldom found in cultivated soils.

The relative values for ground limestone an crushed oyster shell of the same degrees of fineness were found to be very similar, athough there is seen again the tendency for the crushed oyster shell to be less reactive.

Experiment III

The purpose of this experiment was to determine the relative neutralizing values of the different grades of liming materials in correcting the acidity developed in soils through the use of ammonium sulfate fertilizer. A Cecil sandy loam of pH 5.50 was used in 2-gallon pots in the greenhouse. At the beginning of the experiment, in November, 1927, the liming materials were applied in amounts slightly more than sufficient to correct the acidity due to ammonium sulfate, which was to be added at the rate of 1000 pounds an acre to each of the first two crops grown. According to previous work (14), this

amount of ammonium sulfate requires 2,400 pounds of pure precipitated calcium carbonate to neutralize the acidity developed. In this experiment it seemed desirable to add more than this amount, and, therefore, 4,000 pounds of the various materials were added. As will be seen in table 9, however, the actual

TABLE 7

H-ion concentration of an extremely acid Susquehanna clay after various periods of reaction with different kinds and grades of liming materials in greenhouse pots

LIMING MATERIALS				H-ION CONCENTRATION OF SOIL AFTER			
Kind	Grade	Amount to the acre		1 month	3 months	6 months	12 months
		Actual	Equiv. pure $CaCO_3$				
		pounds	*pounds*	*pH*	*pH*	*pH*	*pH*
Check	...	...	...	4.60	4.70	4.48	4.63
Precipitated $CaCO_3$	...	4,000	4,000	4.90	4.95	4.83	4.83
Precipitated $CaCO_3$	...	12,000	12,000	5.15	5.20	5.10	5.08
Precipitated $CaCO_3$	...	20,000	20,000	7.10	5.60	5.43	5.43
Ground limestone	Coarser than 20 mesh	20,000	16,980	4.65	4.80	4.83	4.90
Ground limestone	20 to 60 mesh	20,000	16,340	4.95	5.30	5.15	5.18
Ground limestone	60 to 100 mesh	20,000	16,040	6.30	5.30	5.10	5.08
Ground limestone	Finer than 100 mesh	20,000	16,000	6.35	5.20	5.10	5.13
Crushed oyster shell	20 to 60 mesh	20,000	18,480	4.95	5.20	5.33	5.43

TABLE 8

Relative values of various grades of ground limestone and crushed oyster shells after various periods of reaction with a very acid Susquehanna clay

LIMING MATERIALS			RELATIVE VALUES BASED ON PRECIPITATED $CaCO_3$ AS 100, AFTER			
Kind	Grade	Amounts to the acre as equiv. $CaCO_3$	1 month	3 months	6 months	12 months
		pounds				
Ground limestone	Coarser than 20 mesh	16,980	4	9	24	37
Ground limestone	20 to 60 mesh	16,340	35	86	81	89
Ground limestone	60 to 100 mesh	16,040	103	88	75	78
Ground limestone	Finer than 100 mesh	16,000	106	75	75	84
Crushed oyster shell	20 to 60 mesh	18,480	31	65	95	108

equivalent amount of calcium carbonate was less than this due to the impurity of the materials.

Each liming treatment was in duplicate. The crops, in the order grown, were oats, corn, and Austrian winter peas. The oat and corn crop received 1,000 pounds of ammonium sulfate, 1,000 pounds of superphosphate, and 100 pounds of muriate of potash to each acre of 2,000,000 pounds of soil. The Aus-

trian winter peas received the same amount of superphosphate and muriate of potash as the first two crops, but received only 28 pounds of nitrogen, one-half from potassium nitrate and the remaining half from ammonium nitrate. This latter combination of nitrogen fertilizers was such as not to effect the acidity of the soil.

The pots were moistened with rain water throughout the experiment. At the time of harvest, the crops were removed, dried, and their dry weights

TABLE 9

Yield of Austrian winter peas, and H-ion concentration of a soil fertilized with ammonium sulfate and limed with various kinds and grades of liming materials

LIMING MATERIALS				H-ION CONCENTRATION OF SOILS AFTER REMOVAL OF CROPS			YIELD OF AUSTRIAN WINTER PEAS (DRY WEIGHT)
Kind	Grade	Amounts to the acre		Oats April, 1928	Corn July, 1928	Austrian winter peas February, 1929	
		Actual	Equiv. pure $CaCO_3$				
		pounds	*pounds*	*pH*	*pH*	*pH*	*grams*
Check*	...	...	...	5.50	5.45	5.40	...
Check	...	...	...	...	4.53	4.25	4.4
Precipitated $CaCO_3$	...	1,000	1,000	5.58	5.00	4.75	14.5
Precipitated $CaCO_3$	...	2,000	2,000	6.18	5.43	5.23	18.0
Precipitated $CaCO_3$	...	4,000	4,000	7.20	6.55	6.10	18.5
Ground limestone	Coarser than 20 mesh	4,000	3,400	5.43	5.05	4.88	16.8
Ground limestone	20 to 60 mesh	4,000	3,270	5.83	5.25	5.50	18.0
Ground limestone	60 to 100 mesh	4,000	3,210	6.48	5.65	5.63	19.6
Ground limestone	Finer than 100 mesh	4,000	3,200	6.40	5.70	5.65	18.5
Crushed oyster shell	Coarser than 20 mesh	4,000	3,950	5.25	4.85	4.80	10.0
Crushed oyster shell	20 to 60 mesh	4,000	3,700	6.18	5.60	5.85	19.2
Crushed oyster shell	60 to 100 mesh	4,000	3,570	6.58	5.93	5.83	21.2
Crushed oyster shell	Finer than 100 mesh	4,000	3,450	6.58	6.03	5.88	18.6
Marble dust	Finer than 100 mesh	4,000	4,000	6.70	6.23	6.10	20.3
Regular basic slag	Unassorted	4,000	2,820	6.40	5.73	5.68	20.8
Low grade basic slag	Coarser than 20 mesh	4,000	2,550	5.38	4.95	4.93	17.2
Low grade basic slag	20 to 60 mesh	4,000	2,900	6.00	5.50	5.48	19.3

* This check received no treatment. The second check received the same fertilizer treatment as all other pots, but received no liming materials.

recorded. Soil samples were taken after the removal of each crop for determinations of H-ion concentration.

The H-ion concentration data and the yields of Austrian winter peas are given in table 9. The yields for the first two crops are not given, since there was little difference in the yields obtained from the various lime treatments, because oats and corn are not very acid-sensitive crops. The yield of Austrian winter peas, given in the last column, shows that the coarse grade liming materials

have been beneficial in neutralizing some of the acidity developed by ammonium sulfate. The average yield of the pots receiving the fertilizers and no lime was 4.4 gm., whereas that from the pots receiving in addition to the fertilizers, ground limestone coarser than 20 mesh, was 16.8 gm. The yield from the pots receiving crushed oyster shell coarser than 20 mesh was 10 grams.

In table 10 are given the relative neutralizing values of the various liming materials as calculated from the H-ion concentration data and from the crop-yield data. If the values based on the H-ion concentration data are first considered, it will be noted that the coarse grades of materials have been quite reactive. After 16 months, the ground limestone coarser than 20 mesh gave a relative value of 37 when compared with precipitated calcium carbonate as

TABLE 10

Relative neutralizing values of various grades and kinds of liming materials when used to correct the acidity developed from the use of ammonium sulfate fertilizer

LIMING MATERIALS		H-ION CONCENTRATION OF SOIL SIXTEEN MONTHS AFTER LIMING	RELATIVE NEUTRALIZING VALUES AFTER 16 MONTHS, BASED ON A VALUE OF 100 FOR $CaCO_3$	
Kind	Grade		Calculated from pH data	Calculated from yield data
		pH		
Ground limestone	Coarser than 20 mesh	4.88	37	49
Ground limestone	20 to 60 mesh	5.50	80	61
Ground limestone	60 to 100 mesh	5.63	88	100+
Ground limestone	Finer than 100 mesh	5.65	93	100+
Crushed oyster shell	Coarser than 20 mesh	4.80	28	19
Crushed oyster shell	20 to 60 mesh	5.85	93	100+
Crushed oyster shell	60 to 100 mesh	5.83	95	100+
Crushed oyster shell	Finer than 100 mesh	5.88	101	100+
Marble dust	Finer than 100 mesh	6.10	100	100+
Regular basic slag	Unassorted	5.68	108	100+
Low grade basic slag	Coarser than 20 mesh	4.93	53	69
Low grade basic slag	20 to 60 mesh	5.48	89	100+
Check	...	4.25	...	...

100. This value is considerably higher than that obtained with any of the other soils studied, except the very acid Susquehanna clay. It corroborates the point previously made that the more acid the soil, the more rapid is the reaction of the coarse grade materials used in liming. The H-ion concentration of the soil which was fertilized but received no lime was pH 4.25, a value considerably higher than those of the other soils.

It is interesting to study the yields obtained in a similar comparative manner. Figure 1 shows graphically, first, the relation between the amounts of precipitated calcium carbonate added and the resulting H-ion concentration of the soil; and second, the relation between the added carbonate and the yield of Austrian winter peas. From the yield data and from the yield curve obtained, the relative values given in the last column of the table were calculated. Thus, the

yield from the use of ground limestone coarser than 20 mesh was 16.8 gm. On the curve this represents the use of 1,650 pounds of precipitated calcium carbonate. Since the calcium carbonate equivalent of the limestone coarser than 20 mesh which was added was 3,400 pounds, it will be seen that this material has a value of 49, as compared with 100 for precipitated calcium carbonate. A comparison of the relative values thus obtained from the yield data with those obtained from the pH data shows only a fair agreement. A better agreement would, no doubt, have resulted had there been more pot replications. This would be especially true for the crushed oyster shell coarser than 20 mesh, where poor duplications were obtained.

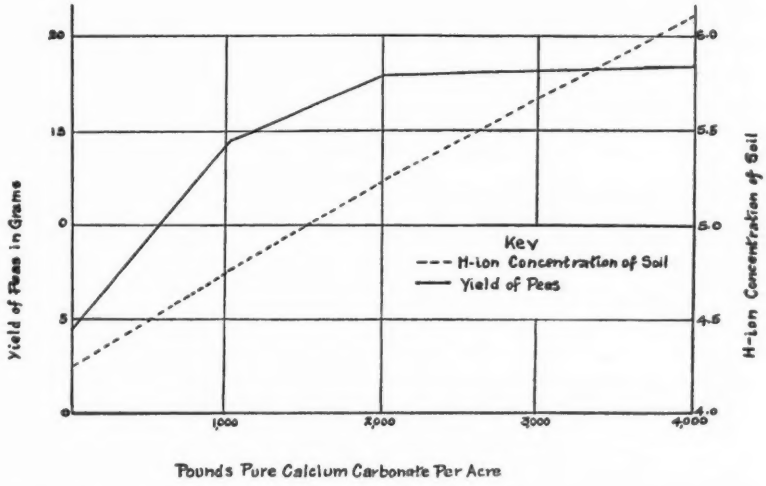
Yield of Peas in Grams
H-ion Concentration of Soil
Key
--- H-ion Concentration of Soil
—— Yield of Peas
Pounds Pure Calcium Carbonate Per Acre

FIG. 1. RELATION BETWEEN THE AMOUNTS OF PRECIPITATED CALCIUM CARBONATE ADDED, THE YIELD OF AUSTRIAN WINTER PEAS, AND THE H-ION CONCENTRATION OF THE SOIL

If the common method of calculating relative values from yield data is used, erroneous values are obtained. This method involves a comparison of the relative increases in yields obtained from the use of equivalent amounts of the various grades of materials, on the basis of 100 for pure, precipitated calcium carbonate. If the value for ground limestone, coarser than 20 mesh, is calculated by this method, a value of 88 is obtained. Similarly calculated, the value for crushed oyster shell, coarser than 20 mesh, would be 40. These values are very much higher than those calculated from the H-ion concentration results. They illustrate the error, previously mentioned, that may be involved in calculating the relative values of different grades of limestone from increases in yields obtained from the use of one uniform rate of application of the various materials. Figure 1 shows graphically the reason for such errors.

The yields from the addition of calcium carbonate increase very rapidly at first, but as more calcium carbonate is added they increase but little. For this soil and crop, then, any comparison of various grades of limestone added at any uniform rate above 2,000 pounds would give erroneous results. Increased yields of crops can serve to give the relative value of different grades of liming materials if the quantities applied range from an amount that gives a slight increase to an amount that produces a maximum increase.

GENERAL DISCUSSION

The results obtained in this investigation show that the time allowed for reaction, and the H-ion concentration of the soil are two factors which affect the neutralizing value of liming materials of different degrees of fineness. Naturally, the longer the time allowed for reaction the greater is the neutralizing value of the coarse grade materials. The greatest rate of reaction of the coarse materials was found to be within the first six months or the first year; thereafter it was very slow. Thus, in case of the medium acid soils, the ground limestone coarser than 20 mesh gave an average value, based on pure calcium carbonate as 100, of 18 after 13 months, and of only 21 after 2 years. Similarly the value of this material with the very acid Cecil sandy loam was 17 after 6 months, and 18 after a year. In the case of the very acid Susquehanna clay, however, there was considerable reaction between six months and a year, no doubt because this soil is extremely acid. The same slow rate of reaction after the relatively high initial rate was also found for the 20- to 60-mesh material. The average value of the 20- to 60-mesh limestone with the two medium acid soils was 46 after 6 months, 64 after 13 months, and 60 after 2 years. With the Cecil sandy loam the values obtained for the same material were 76 after 3 months, 75 after 6 months, and 73 after 12 months; and with the Susquehanna clay the values for the same periods were, 86, 81, and 89, respectively.

The reason for this slow rate of reaction after the high initial rate is not entirely clear. It probably is partly because the finer materials of the grade react very quickly as compared with the coarser particles present, or it may be that a part of the limestone is more porous and more easily decomposed than the rest. It would be expected, of course, that the rate of reaction would decrease with time because the soil is gradually getting less acid, but that this is not the controlling factor is shown by the fact that where two rates of application were used, as in experiment II, the same phenomenon was observed with the low rate as with the high rate.

No doubt, the coarse grade materials will continue to react slowly with time. It is, therefore, planned to continue this experiment over a period of years to determine to what extent and at what rate this reaction will take place.

That the initial acidity of the soil is a controlling factor in regard to the amounts of coarse grade materials reacting after various periods of time has been well shown. For example, the 20- to 60-mesh limestone gave a value with medium acid soils of 25 after 4 months, whereas after 3 months it gave a value of

76 with a very acid Cecil sandy loam, and of 86 with an extremely acid Susquehanna clay.

Interesting comparisons can also be made of the relative rates of reaction of the various grades of materials on the same soil. Thus, with the two medium acid soils, it took about four months for the 20- to 60-mesh limestone to give the same value as was obtained from the 60- to 100-mesh limestone in 15 days; and whereas the latter had completely reacted in less than 6 months, only about 60 per cent of the former had decomposed after 2 years.

Although a comparison of these results directly with those obtained by other investigators is difficult because of the different methods and grades of materials used and the different periods of time allowed for reaction, some comparisons can be made. In this investigation, as has been pointed out, the 20-mesh limestone gave a value of about 20 with medium acid soils after a period ranging from 1 to 2 years, while after 1 year it gave a value of 37 with a very acid soil. MacIntire and Shaw (11) found that after 4 years only 6½ per cent of the 10- to 20-mesh limestone used in their experiment had decomposed. Their lower value can probably be explained by the fact that their soil was only slightly acid.

The values obtained by the Pennsylvania workers are much in line with those herein reported. Thus, White and Gardner (22) found that after 3 years only 14.9 per cent of the 8- to 12-mesh limestone had undergone decomposition, compared with 46.7 per cent of the 20- to 40-mesh limestone.

The results of Rost and Fieger (17) on field soils can also be roughly compared with the data just presented. A calculation of their results shows that the average reduction in H-ion concentration from the ground limestone coarser than 20 mesh with four sandy soils, 2 years after liming, gives values of 22 and 32 for the two different rates of application as compared with the finely ground limestone valued at 100. Very similar values were obtained with a Carrington silt loam.

It is evident that the rates of reaction of the other liming materials used in this study are also influenced by their degree of fineness and by the acidity of the soil. The crushed oyster shells gave much the same values as did the ground limestone of the same degrees of fineness, although with the coarser grades the limestone seemed slightly more effective.

The regular basic slag, containing 18 per cent phosphorus pentoxide, gave values of about 70 after 1 year and about 80 after 2 years with the medium acid soils. With the soil made very acid through the use of ammonium sulfate, the value obtained after 16 months indicated a complete reaction. In other words, the latter soil was so acid that the slag reacted with it to the same extent as it did in the laboratory with boiling 0.4 *N* HCl. It would seem, therefore, that about 20 to 30 per cent of the basic material found in the slag is very slowly reactive. In a former publication (14) in which the material reacted with the soil for about 2 years, it was found that for a unit weight its value in correcting soil acidity was about 55 per cent of that of pure precipitated

calcium carbonate. Since its calcium carbonate equivalent as measured against 0.4 *N* HCl acid was found to be 70.6, the value as calculated in this investigation would be 78, a value similar to that found after 2 years of reaction, in this study.

The low grade slag, containing only about 11 per cent phosphorus pentoxide was found to be less reactive than the high grade material. This was because of the higher amount of coarse material found in this slag. The material coarser than 20 mesh was found to be slightly more reactive than ground limestone or crushed oyster shell of similar grade. The 20- to 60- mesh slag was far less reactive than the 20- to 60-mesh limestone and was found to bear about the same relationship to the latter that the regular slag bears to the finely divided limestone of similar grade.

In applying the data presented in this investigation to field conditions, several considerations arise. In the first place, the reaction between the soil and the liming materials in greenhouse pots continued throughout the year, whereas in the field the ground is frozen during a part of the year. Although this is a relatively short period in the southern states, it is several months in the northern states. Therefore, the rate of reaction especially for the coarse grade materials would probably be lower than that found in these experiments.

There is also the question of the downward movement of lime in field soils. A point sometimes made in favor of ordinary ground limestone rather than finely divided material is that there is more leaching in the latter case. Some unpublished results obtained by the writer, however, indicate that if the same pH value is obtained from the coarse grade materials through the use of larger amounts, the downward movement of the lime in the two cases is about the same. Therefore, the results of pot experiments should not be different in this respect from those with soils in the field.

Another point that may be raised is what difference one might expect in the decomposition of the coarser grade materials when applied alone, as was done in most cases in this experiment, and their decomposition when they are applied in a mixture containing finer material. It might be expected that their decomposition would be slower in the latter case. There is no indication from a calculation of some of the data presented, however, that such is the case. In experiment I, values were obtained from the various grades of materials when used alone and when used in a mixture. If the percentage of the various grades represented in the mixture are multiplied by the values obtained from the respective grade when used singly, and the products thus obtained are added, the resulting figure is smaller than that obtained by multiplying by 100 the value obtained for the mixture. This indicates that the coarse grade materials have probably been as reactive when used in the mixture as when used alone.

If definite values are obtained, therefore, for the various grades of material after various periods of time, it should be possible to evaluate the rate of reaction of any ground limestone, if its mechanical analysis is given. In doing this, however, it must be remembered that dolomitic limestone, as has been

shown by a number of investigators, is less readily reactive than calcium limestone.

SUMMARY

This investigation consists of a study of the reaction, after various periods of time, of ground limestone, crushed oyster shell, and basic slag of different degrees of fineness, with soils in greenhouse pots, especially as influenced by the hydrogen-ion concentration of the soil.

The results may be briefly summarized as follows:

1. The greater the H-ion concentration of the soil, or the greater the avidity of the acids, the higher is the rate of reaction of liming materials with it.
2. The finer the liming materials added, the quicker will the soil acids be neutralized.
3. Ground limestone coarser than 20 mesh is very slowly reactive. With medium acid soils it gave a value of about 20 after 2 years as compared with a value of 100 for precipitated calcium carbonate, and with an extremely acid soil the value was 37 after 1 year.
4. The 20- to 60-mesh limestone gave values on the medium acid soils after 2 years of about 60, whereas with two very acid soils it gave values of about 88 after 1 year.
5. Crushed oyster shells gave about the same neutralizing values as the ground limestone of the similar grades of fineness, although the coarse grade shells seemed slightly less effective than the coarse grade limestone.
6. The neutralizing value of the ordinary basic slag as measured against boiling 0.4 *N* HCl was found to be completely effective in neutralizing the acidity of a very acid soil. With the medium acid soils, however, it was found that after 2 years only about 80 per cent of its potential neutralizing value is effective.
7. The low grade basic slag, which contains considerable coarse material, was found to be much less reactive than the finer, ordinary basic slag. On the basis of equal potential neutralizing value it was found to be about 80 per cent as effective as the latter.
8. The use of ground limestone and crushed oyster shell coarser than 20 mesh was effective in neutralizing some of the acidity developed by the use of ammonium sulfate fertilizer, and in maintaining the yields of Austrian winter peas.

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BOOK REVIEWS

Colloid Chemistry; Principles and Applications. By JEROME ALEXANDER. D. Van Nostrand Co., Inc., New York, 1929. Pp. viii + 270.

This is one of a series of industrial chemical monographs edited by W. Lee Lewis and Harrison E. Howe. In the preface to the first edition, which appeared in 1918, the author explained that his treatise "was the result of an attempt to compress within a very limited space the most important general properties of colloids, and some of the practical applications of colloid chemistry." A revised and enlarged edition appeared in 1924. In the present edition, which is the third, there are included the more recent findings of colloid chemists. The book contains 14 chapters, an appendix, bibliography, glossary, and author and subject indexes. The topics dealt with include: Material units and the forces dominating them; Classification of colloids; Consequences of subdivision; The ultramicroscope; General properties of colloids; Practical applications of colloid chemistry.

The Structure and Life of Forest Trees. By M. BÜSGEN AND F. MÜNCH, Translated by THOMAS THOMSON. John Wiley and Sons, Inc., New York, 1929. Pp. xi + 436, figs. 173.

The first German edition appeared in 1897 under the title "Bau und Leben unserer Waldbäume." The author, M. Büsgen, prepared also a second edition which was published in 1917. After his death, in 1921, the book was revised and enlarged by E. Münch, professor in the Forest Academy at Tharaud, and was published as the third edition in 1926. The translator states in his preface that: "During recent years many valuable works have appeared both in England and America on silviculture, forest management, and other branches of forestry, but there is, so far, no book dealing comprehensively with the structure and life of forest trees."

There are 14 chapters dealing with: The form of the tree; The buds; Properties and life processes of the meristem of the tree; The elements of the xylem; The tree rind; The annual ring; Anatomical basis of the technical properties of timbers; The leaves; The root; Water economy of the tree; The mineral nutrients; Movements and transformations of substances in the body of the tree; Flowers, fruits, and seedlings; Local races. There is an author and subjects index and a list of common and scientific names of plants mentioned in the text.

Plant Ecology. By J. E. WEAVER AND F. E. CLEMENTS. McGraw-Hill Book Co., Inc., New York and London, 1929. Pp. xx + 520, figs. 262.

The book was written, according to the authors, "from the standpoint of

development, instrumentation, and experiment. The student of plant production, whether in botany, agriculture, grazing, forestry, plant pathology, or other fields, is beginning to study more thoroughly the intimate relations between plants or groups of plants and their environment. In fact, many of his most important problems deal with the relations of plant to habitat, whether the latter be natural or modified by cultivation, and these can not be satisfactorily solved until these relationships are well understood."

The 18 chapters of the book are devoted to the following subjects: Vegetation; its origin, development, and structure; Methods of studying vegetation; The units of vegetation; Plant succession; Initial causes of succession; Aggregation, migration, and ecesis; Competition and invasion; Reaction and stabilization; Factors of the habitat; the soil; Relation of underground plant parts to environment; Humidity, wind, and evaporation; Temperature; Light; Plant response as a measure of environment; Adaptation to water; Relations between plants and animals; Plants and plant communities as indicators; Climax formations of North America.

A bibliography of 606 numbers adds to the value of the book for classroom and reference purposes. The paper, illustrations, and binding are in keeping with the high standards set by the pubishers.

Microbiology. By B. F. LUTMAN. McGraw-Hill Book Co., Inc. New York and London, 1929. Pp. x + 495, figs. 211.

The author states in the preface that the "general scheme of presentation has been to describe types in considerable detail; a method borrowed from the zoölogists. Types have been chosen which are common and have biological or practical importance, if possible, both. As much as possible of both morphology and physiology has been connected to some type of mold, yeast, bacterium, or enzyme, and other facts described in terms of the types."

Although the book is primarily intended for use in the classroom, it should have distinct value for general reference in the field of microbiology. Either because of the method of treatment, or the wide extent of the field to be covered, the author makes but scant mention of a number of relatively important topics. For instance, the decomposition of cellulose and the fixation of elementary nitrogen are dealt with inadequately. On the other hand, the topic "modern attacks on the constancy of species" is discussed in sufficient detail to give the beginner in microbiology a satisfactory insight into questions that are both interesting and important.

Die Bodenazidität. By H. KAPPEN. Julius Springer, Berlin, 1929. Pp. vii + 363, figs. 35 and 1 color plate.

The subject of soil acidity has grown in interest because of the more intensive methods of soil treatment and the increasing use of chemical fertilizers. The author states in his preface that it was not his purpose to write a monograph on soil acidity including a review of the literature pertinent to the subject

but rather to develop a fundamentally sound and, at the same time, lucid exposition of the essential facts of soil acidity. The more important questions considered by the author include: The nature of acidity in mineral soils; Soil reaction; Determination of soil reaction; Behavior of acid soil toward acids and bases; its neutralization or buffer capacity; Behavior of acid soils toward solutions of salts; The absorption capacity of acid soils; The relation of increasing acidity to the physical properties of soils; The influence of reaction on soil microörganisms; The plant physiological significance of soil reaction; Occurrence and extent of soil acidity; The influence of manures and fertilizers on soil acidity; The use of lime for repairing the damage done by soil acidity; The use of chemical fertilizers on acid soils.

J. G. LIPMAN.

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JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

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FACTORS AFFECTING THE ESTIMATION OF LIME REQUIREMENT FROM pH VALUES

M. F. MORGAN

Connecticut Agricultural Experiment Station

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The use of pH values as a measure of soil reaction has developed from a complicated laboratory technique employed in a very few experiment station research laboratories 10 years ago to a nearly universally employed routine determination. It is used not only by the investigator but by the extension specialist, farm advisor, and by an increasing number of practical growers of both fancy and staple crops. Although there are many differences in detail as to the method employed, the results obtained are comparable in their expression of the actual hydrogen-ion concentration of the soil in terms of pH.

As yet we cannot state whether the injurious effects of soil acidity (in its broader sense) upon the growth of most economic crops is a direct function of the hydrogen-ion concentration or whether the depression of favorable biological activities in the soil, the higher concentrations of soluble aluminum and manganese, or the lower quantities of replaceable calcium or other bases may be the factor or factors which should be properly charged with adversely affecting the crop on acid soils. However, there is a general correlation of these various soil acidity phenomena with the intensity of soil acidity as measured in terms of pH. Since its measurement is relatively simple and accurate, it will continue to be more widely employed, to the point where few progressive farmers will be ignorant of the soil reaction of any cultivated field.

Yet the measurement of soil acidity in terms of pH makes no direct expression of the quantity of liming material which is required to change the reaction to a desired more favorable one. A measure of the temperature of a room, as, for instance, 40°F., does not express directly the amount of heat required to bring the air in the room to, say, 70°F. Yet we can easily make such a calculation, if humidity, pressure, and insulation are also known.

In our older methods of measurement of soil acidity the results were expressed in terms of "lime requirement"; in other words, of the number of pounds or tons of CaO or $CaCO_3$ required to bring an acre of surface soil to conditions of approximate neutrality. There were wide discrepancies between the figures obtained by different methods, as was clearly pointed out by Stevenson (26). Yet some of them, such as the Veitch (30) and Jones (16) methods in this country, and the Hutchinson-MacLennon (13) method in Europe, gave

results which compared favorably with the amount of lime required in actual practice to neutralize the soil.

Since the measurement of pH is more rapid and simple than most lime requirement methods, and gives results which much more directly express the degree of severity of the various adverse factors associated with soil acidity, it is now more widely employed than the methods which measure acidity directly in terms of "lime requirement." It would be of much added value if we could use the pH test to determine this "lime requirement" as well.

This article is submitted as evidence that, for practical purposes, it is possible to calculate with reasonable accuracy the amount of lime or limestone required either to bring the soil to the neutral point, or to bring it to some desired less acid condition than that existing.

PREVIOUS INVESTIGATIONS

In a number of cases there has appeared to be a direct correlation between lime requirement and hydrogen-ion concentration, as expressed in pH values, in comparisons of a particular soil at varying degrees of acidity. Thus Blair and Prince (3), in comparing pH with lime requirement by the Veitch method, found a close relationship when testing different plots of the same soil type, which had been variously treated. They suggested that pH measurement might be made to serve as a lime requirement method. In a later publication (4) they state: "for normal soils a determination of pH values may be of considerable assistance in arriving at the amount of lime required for general farm crops."

Burgess (6), in comparing the effects of past fertilizer treatments in field plots at the Rhode Island Experiment Station, found a fair correlation between acidity as indicated by pH values and the Jones lime requirement.

Johnson (15), working with soil of various types, found "no relationship . . . between the Veitch lime requirement and pH. The Truog (28) method of estimating lime requirement gave a slight correlation. With soil of similar type there appeared to be a relationship between the apparent quantity and strength of soil acids. Since clay and organic matter act as buffers in keeping the hydrogen-ion concentration down, soils of different types with respect to these buffer substances would be expected to give different results."

Parker and Bryan (10), in comparing the pH, the Truog lime requirement, and the hydrolysis of ethyl acetate, found a fairly good correlation in the 42 soils under comparison.

Wherry (31) attempted to calculate lime requirement from the hydrogen-ion concentration as expressed as specific acidity by the equation "Lime Requirement = C (Specific acidity—1)."

The value C was believed to be a measure of the absorptive power of soil colloids for the OH-ion. He concluded that it was impractical to calculate the lime requirement from acidity determinations in general.

Trénel (27), in comparisons between the pH of soil suspensions containing potassium chloride and the lime requirement as determined by electrometric titration, published curves which suggested a dependence of pH upon lime requirement.

Jensen (14), in an investigation of the acidity of 115 Danish fields, concluded that a single pH determination is inadequate for computing the lime requirement. Contrary to practical experience, sandy soils appeared to require more lime than loamy soils for a change in reaction. Loamy soils required more lime than sandy soils for the neutralization of exchange acidity as determined by the potassium chloride method.

Carleton (7), in a comparison of pH value with the Jones lime requirement of Quebec soils, found that soils of various types exhibited no correlation, whereas soil of the same textual character gave indications of correlation.

Saint (23), in a comparison between pH, the thiocyanate color test for estimating acidity developed by Comber (8), and the lime requirement by the Hutchinson-MacLennon method, found only a rough correlation for the soils examined. It was found that when the heavy and light soils were tabulated separately the results were much more consistent, the heavier soils giving higher lime requirements at the same pH values than the lighter soils. Organic matter also appeared to increase the lime requirement. When adjoining fields on the same farm were compared, there was a definite correlation between the lime requirement and the pH.

Arrhenius (1) has presented the following table, which attempts to predict the amount of lime or hydrated lime in kilograms per hectare which is required to change the soil reaction 1 pH unit in the alkaline direction:

SOIL TEXTURE	HUMUS CONTENT		
	Poor	Average	Rich
Sandy	500	1,000	1,500–3,000
Fine sandy	500–1,000	1,000–1,500	2,000–3,000
Light clay	1,500	2,500	3,500
Average clay	2,500	3,500	4,000
Heavy clay	3,000	4,000	4,500

Humus soils with 15 per cent organic matter—4,000–8,000

METHODS OF INVESTIGATION

Since the Jones lime requirement method has been tentatively recommended by the Association of Official Agricultural Chemists (17) and our experiences with this method for a number of years have led us to believe that it gives with reasonable accuracy the amount of lime required to bring the soil nearly to the neutral point, it was selected as a basis for comparison with the pH results.

The technique used was the modification of the Jones method proposed by Dorsey (9). Calculations were made on the basis of $CaCO_3$ requirement in pounds or tons for 2,000,000 pounds of soil.